Journal of Hazardous Materials Advances 5 (2022) 100047

Contents lists available at ScienceDirect

Journal of Hazardous Materials Advances

journal homepage: www.elsevier.com/locate/hazadv

Application of catalytic hydrodehalogenation in drinking water treatment for organohalogenated micropollutants removal: A review

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

Chemical Engineering Department, Universidad Autónoma de Madrid, Ctra. Colmenar km 15, 28049 Madrid, Spain

ARTICLE INFO

Keywords:
Catalytic hydrodehalogenation
Water treatment
Micropollutants
Drinking water
Organohalogenated compounds

ABSTRACT

This study presents an overview on the application of catalytic hydrodehalogenation (HDH) as a potential polishing step for organohalogenated micropollutants removal during drinking water treatment. Stringent regulations for drinking water quality require the development of innovative processes to increase the efficiency of conventional Drinking Water Treatment Plants (DWTPs). Recently, HDH has appeared as a promising technology for such goal. This process can be operated under ambient conditions within a wide range of organohalogenated micropollutants concentrations, allowing to significantly decrease the toxicity of the treated water. Despite its effectiveness, the performance of the technology can be affected by the nature of the micropollutant. Pharmaceuticals, pesticides and disinfection by-products, among other, have been herein considered to evaluate the impact of the pollutant nature on the performance of the process. The impact of both the active phase and the support that constitute the catalysts commonly used in HDH has been also analyzed in detail, considering not only the commonly used precious metal-based catalysts (Pd, Rh, Pt) but also innovative and less expensive catalysts like Fe, Ni and bimetallic catalysts. Special attention has been also given to study catalyst deactivation and the development of regeneration procedures. To analyze the feasibility of the HDH treatment, its application in real complex aqueous matrices such as mineral, tap and surface water has been also considered. Furthermore, the possible integration of HDH in a conventional DWTP has been discussed, and the scaling-up of the technology using robust structured catalytic reactors has been finally addressed.

1. Introduction

Water is a limited natural resource that is exposed to a large diversity of pollutants that can limit its use in different sectors. Among the most common pollutants, the so-called pollutants of emerging concern or micropollutants have aroused special interest in recent years. Despite appearing at low concentrations in water (in the range of ng L^{-1} to μg L^{-1}), they could cause adverse effects on the environment, on aquatic organisms, and, ultimately, on human health (Luo et al., 2014). These micropollutants usually end up in the sewage networks and, finally, reach Wastewater Treatment Plants (WWTPs). In these facilities, water is subjected to different physico-chemical and biological treatments, which are not totally effective to reach the complete elimination of these compounds. Accordingly, WWTP discharges represent one of the main sources of emerging pollutants to natural watercourses. Apart from the environmental impact, this situation is of particular concern when freshwater is collected for consumption since most of them are harmful to human health (Jones et al., 2005; Padhye et al., 2014).

Water used for human consumption must ensure several quality standards such as being colorless, odorless, and tasteless. It must also contain an adequate concentration of oxygen and dissolved salts and, of course, be free of pathogenic microorganisms and harmful chemicals. To obtain water suitable for consumption, natural water from aquifers, wells, rivers, reservoirs and lakes is subjected to a purification process in which physico-chemical treatments are mainly applied in order to improve its quality and thus, to comply with the parameters established by the regulation (Benner et al., 2013). Drinking Water Treatment Plants (DWTPs), whose general scheme is collected in Fig. 1, are the facilities intended for such goal. Pre-treatment, mainly based on physical processes, allows to separate large objects that could create obstructions along the water treatment path. Pre-oxidation is afterwards applied, commonly using chlorine agents due to their low cost. Its main aim is the removal of dissolved organic matter as well the reduction of the suspended solids content and the microbiological load. Clarification of water takes then place by consecutive coagulation-flocculation, sedimentation, and filtration processes, which remove turbidity and fine residual solids. Finally, pH is neutralized, and a disinfection step is afterwards applied to warrant the biological quality of water and prevent the growth of microorganisms along the whole distribution network. Usually, this last step is carried out with chlorinated derivatives, such as chloramine (Benner et al., 2013).

---

* Corresponding authors.
E-mail addresses: julia.nieto-sandoval@uam.es (J. Nieto-Sandoval), macarena.munnoz@uam.es (M. Munoz).

https://doi.org/10.1016/j.hazadv.2022.100047
Received 28 October 2021; Received in revised form 4 January 2022; Accepted 15 January 2022

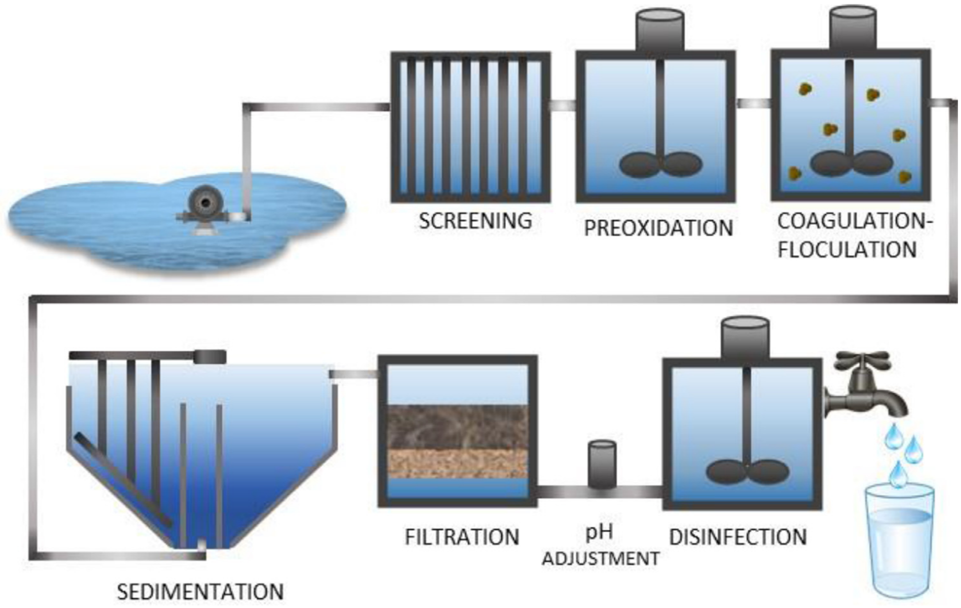


Fig. 1. Conventional drinking water treatment plant scheme.

Drinking water quality in the European Union is regulated by the Directive 98/83/CE, which was later modified by the Directives 2015/1787/EU and 2020/2184/EU. This regulation establishes the sanitary criteria for the quality of water for human consumption and reflects, among other specifications, the type of analysis and sampling frequency of the regulated parameters (microbiological, chemical and general indicators), as well as their threshold limit values.

2. Organohalogenated micropollutants occurrence in DWTPs

Conventional drinking water treatments do not allow to reach the complete elimination of a wide variety of micropollutants (Benner et al., 2013; Vieno et al., 2007). Among them, organohalogenated compounds are of increasing concern since they are characterized by a high toxicity, low biodegradability and superior bioaccumulation potential (McHugh et al., 2010; Ozturk, 2018). The presence of a halogen substituent on the organic molecules structure is the main reason behind their hazardous properties. For example, the EC_{50} value (Microtox assay) obtained for the chlorpromazine drug was almost one order of magnitude lower than its analog chlorine-free compound, promazine (3.3 and 26.8 mg L^{-1}, respectively) (Nieto-Sandoval et al., 2019a). In the same line, toxicity of a triclosan solution (EC_{50} of 0.25 mg L^{-1}) analyzed by Microtox test using *Vibrio fischeri* decreased from 12 TUs to a negligible value after the initial compound was completely dechlorinated (Nieto-Sandoval et al., 2019b).

Despite their hazardous properties, most organohalogenated micropollutants are not considered in the regulation, and have been detected in drinking water worldwide (Huerta-Fontela et al., 2011; Padhye et al., 2014). These compounds have a varied origin, but they can be generally classified in three main groups: pharmaceuticals, pesticides and personal care products. Apart from them, the presence of undesired disinfection by-products (DBPs) usually formed along the drinking water treatment process is of increasing concern given their halogenated (and hazardous) nature. Table 1 collects the organohalogenated compounds detected in aqueous matrices related to drinking water treatment from different locations and their DWTP removal efficiencies.

2.1. Pharmaceuticals

Pharmaceuticals are a wide group of chemical substances designed to prevent and cure diseases of both animals and humans. Their widespread consumption, due to the increasing population and technological development, has promoted their introduction in the aqueous medium (Huerta-Fontela et al., 2011). The main sources of pharmaceuticals into the aqueous environment are domestic, hospital and industrial waters as well as those discharged from activities like aquaculture and livestock. Population is exposed to pharmaceuticals through drinking water and, overall, through the consumption of meat and fish (Gavrilescu et al., 2015). Although they appear at very low concentrations, their potential effects through chronic exposure are of increasing concern (Huerta-Fontela et al., 2011; Reis et al., 2019). Despite this fact, these compounds have not been included in the legislation for drinking water, even in the most recent Directive 2020/2184/EU.

Pharmaceuticals occurrence in natural waters depends significantly on the location, trends of consumption, climatic conditions, or advance technologies implementation, being their overall removal in DWTPs diverse. For instance, complete removals were achieved for the non-halogenated erythromycin or sulfamethoxazole while values of 82% and 61% were obtained for the organohalogenated compounds diclofenac and loratadine, as shown in Table 1 (Huerta-Fontela et al., 2011). Wing et al. (2013) monitored 32 pharmaceuticals from tap water of 13 cities in China, being caffeine, metronidazole, salicylic acid, clofibric acid, carbamazepine and dimetridazole those that appeared more frequently ($\geq$ 20% of samples). All in all, due to their high persistence, many organohalogenated pharmaceuticals have been detected in drinking water tap in EU countries. For instance, diclofenac has been detected at 10 ng L^{-1} in Germany and the antibiotic thiamphenicol at 49 ng L^{-1} in China (Liu et al., 2019; Lonappan et al., 2016).

2.2. Pesticides

Organohalogenated compounds are commonly used in the formulation of pesticides and herbicides due to their strong biocidal character. These compounds, used since the nineteenth century, have evolved over the years to more selective and persistent products. In the last decades, neonicotinoid pesticides emerged as possible substitutes for traditional ones, as they have less toxicity towards mammals, birds and fish (Tomizawa and Casida, 2005). However, nowadays, they are of great concern because their association with increased bee mortality and, in fact, they have been recently included in the EU Watch List (Decision 2018/840) (Whitehorn et al., 2012).

Pesticide exposure through drinking water is of particular concern since it is related to serious human effects such as gastroin-

Table 1
Organohalogenated compounds quantified in real water matrices and removal efficiencies achieved in DWTP.

Type	Compound	Concentration (ng L^{-1})	Place	DWTP removal (%)	Reference
Pharmaceuticals	Chlorpromazine	5	DWTP influent, Spain	n.a.	(Huerta-Fontela et al., 2011)
	Diclofenac	113	Surface water, Spain	61	(Jurado et al., 2019; Padhye et al., 2014)
	Loratadine	123	DWTP influent, Brazil	82	(Reis et al., 2019)
Pesticides	Imidacloprid	40	Tap water, USA	77	(Elfikrie et al., 2020; Klarich et al., 2017)
	Acetamiprid	1100	Surface water, Belgium	40	(Sjerps et al., 2019; Wan et al., 2019)
	Tebuconazole	10	DWTP effluent, China	88	(Dong et al., 2021; Elfikrie et al., 2020)
Personal care products	Triclosan	15	Tap water, China	55	(Li et al., 2010; Padhye et al., 2014)
	Triclocarban	13	Tap water, Spain	n.a.	(Carmona et al., 2014)
DBPs*	Dibromoacetic acid	500	Tap water, Croatia	–	(Kurajica et al., 2020)
	Trichloroacetic acid	100	Tap water, Croatia	–	(Kurajica et al., 2020)
	Trichloromethane	1930	Tap water, Spain	–	(Freire et al., 2008)

n.a.= not available.

* DBPs are usually formed during DWTP process, removal not shown (Gilca et al., 2020).

testinal, carcinogenic, respiratory, reproductive and endocrine disrupting, among other (Elfikrie et al., 2020). For these reasons, legislation (Directive 2020/2184/EU) establishes a maximum concentration value of 0.1 μg L^{-1} for individual pesticides, and 0.5 μg L^{-1} for the sum of all of them in drinking water. In addition, aldrin, dieldrin, heptachlor and heptachlor epoxide have been limited to 0.03 μg L^{-1} each.

Pesticides can pollute the water environment through different processes such as adsorption of pesticides by soil particles, their leaching through soil by rain or irrigation water, polluting groundwater, or through runoff, appearing in surface water. In fact, the presence of pesticides in groundwater in Spain is increasingly abundant as a consequence of agricultural activities (Herrero-Hernández et al., 2013) and some organochlorine pesticides that had been prohibited more than 40 years ago are still being detected, such as DDT or cyclodienes, *i.e.* aldrin or endrin, due to their high persistence (Carro et al., 2014). Pesticide pollution of surface and ground water makes them potential candidates to be present in the raw water used for DWTPs. Due to the inefficient removal ability of DWTP processes for their removal, they can be present in final drinking water. As a representative example, it must be noted that only 40% removal has been reported for acetamiprid (see Table 1). Consequently, the presence of neonicotinoid pesticides in tap water is not uncommon. For instance, imidacloprid has been detected in tap water from USA at a concentration of 40 ng L^{-1}, and propiconazole at 38 ng L^{-1} in finished drinking water from Malaysia (Elfikrie et al., 2020; Klarich et al., 2017).

2.3. *Disinfection by-products*

In contrast to the abovementioned micropollutants, disinfection by-products (DBPs) are formed *in situ* along drinking water treatment, particularly in the pre-oxidation stage, which is usually carried out by chlorinated agents (Niu et al., 2016; Williams et al., 2019). These compounds are generated through substitution, addition and oxidation reactions between the disinfectant agent and the natural organic matter (NOM) as well as the halide ions, such as bromides and chlorides, present in the raw water. In the first study reporting the formation of DBPs through water treatment, published in 1974, four types of trihalomethanes (THMs) were identified (Rook, 1974). Several years later, the generation of haloacetic acids (HAAs) was also demonstrated during the drinking water treatment (Christman et al., 1983). The main THMs are chloroform, dichlorobromomethane, dibromochloromethane and bromoform. HAAs consist of nine compounds, although the main ones are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). Depending on the water characteristics, *i.e.* pH, type of NOM (hydrophobic behavior), or the presence of halide ions, different DBPs will be produced. For instance, at high pH values (>7), the formation of THMs predominates whereas HAAs are generated to a minor extent (Hung et al., 2017; Rizzo et al., 2005). Moreover, the presence of bromide ions in the inlet water, usually related to the use of seawater in the toilets flush, can lead to the formation of hypobromous acid (HOBr) along the pre-oxidation step, which can act as a substituent agent for DBPs (Sun et al., 2009). In addition, hydrophobic and high molecular weight NOM contain the major fraction of DBP precursors such as humic and fulvic acids. If more hydrophilic precursors are present, dihaloacetic acids and trihalomethanes would be formed to a greater extent than trihaloacetic acids (Hua and Reckhow, 2007).

DBPs can affect human health in terms of cytotoxicity, mutagenicity, teratogenicity and carcinogenicity (Postigo et al., 2018; Srivastav et al., 2020). In a very recent work, Evlampidou et al. (2020) reported a study collecting data of THMs levels in drinking water from 28 countries, indicating that prolonged exposure to these contaminants is associated with an increased risk of bladder cancer. Specifically, an exposure greater than 25 μg L^{-1} increased the risk by 35% (Evlampidou et al., 2020). Bromine-containing DBPs have been associated with a higher toxic character than the chlorinated ones (Yang and Zhang, 2013). Iodinated DBPs represent a low percentage of the total DBPs in drinking water, but they contribute substantially to the overall toxicity and have not been so far carefully evaluated (Abusallout et al., 2017). Although up to 700 types of DBPs have been identified in the aqueous medium, just a small percentage of these compounds are under regulation for drinking water quality. In this sense, the maximum concentration for the total sum of THMs has been established at 80 μg L^{-1} by the US EPA, while in Europe (Directive 2020/184/EU) it has been fixed at 100 μg L^{-1}. In addition, US EPA, and very recently also the European Union (Directive 2020/2184/EU), have established a maximum concentration in drinking water for the sum of the five HAAs mentioned above at 60 μg L^{-1} (US EPA, 2006). All in all, it is common to detect DBPs in drinking water for human consumption. For instance, dibromoacetic and trichloroacetic acids have been identified in tap water from Croatia at 500 and 100 ng L^{-1}, respectively, while chloroform has been detected at 1930 ng L^{-1} in Spain, as shown in Table 1.

2.4. Other organohalogenated micropollutants

Apart from DBPs, pharmaceuticals and pesticides, there are other groups of organohalogenated micropollutants present in water sources that can also cause a potential impact to human health. Personal care products like perfumes, fragrances, toothpaste, or sun protection agents are used to a large extent in our daily life, and they usually contain persistence chemicals that cannot be completely eliminated in WWTPs. These compounds are introduced into the water environment after incomplete absorption, excretion from body or from industrial wastes (Cizmas et al., 2015; Ebele et al., 2017). For instance, the bactericide agent triclosan, widely used in products such as toothpaste, deodorants or shampoos, appears frequently in surface waters (Singer et al., 2002; Zhao et al., 2010). Since its removal in DWTPs is not complete (55% average), triclosan has even been also detected in tap water in China at a concentration of 15 ng L^{-1} (Li et al., 2010).

Chemical flame retardants, commonly applied in the industry for fire prevention, are also an important group of pollutants of emerging concern. Brominated flame retardants (BFRs), applied to commercial products such as plastics, textiles or electronic circuits, are particularly harmful (de Wit, 2002). Among them, the most common are tetrabromobisphenol A (TBBPA), polybromadodiphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD). Although many of them were regulated since 2003 by EU due to their harmful effects, they are still present in watercourses. Specifically, BDE-209 has been identified in surface waters in England at a concentration of 0.3 µg L^{-1} (Cristale et al., 2013). These compounds are currently replaced by novel brominated flame retardants (NBFRs) and organophosphates (OPFRs), but their toxic nature continues being evidenced and are still detected in finished drinking waters, such as the chlorinated organophosphate TDIP (tris(dichloroisopropyl)phosphate) at a concentration of 70 ng L^{-1} in USA (Cristale et al., 2013; Stackelberg et al., 2007).

Perfluorinated compounds (PFCs), mainly used in detergents or in the Teflon industry, are also of great concern. PFCs have been detected in raw and finished water from DWTPs, achieving a total removal of only 35% (Sun et al., 2018). Among them, perfluorooctane sulfonate (PFOS) and perfluorooctane acid (PFOA) are the most predominant pollutants. In fact, EPA established in 2016 a maximum concentration at 70 ng L^{-1} for the sum of both in drinking water (Cordner et al., 2019).

Finally, chlorinated paraffins, used in the industry as additives in lubricants and plasticizers, show high persistence and bioaccumulative and toxic properties as well. Short-chain chlorinated paraffins (SCCPs) are the most used and, despite their low solubility in water, they have been identified in different watercourses (Bayen et al., 2006). Although data of their occurrence in drinking water has not been found in the literature, SCCPs have been detected in surface water used as source for DWTP in Spain at a concentration of 0.15 µg L^{-1} (Rubirola et al., 2018).

3. Application of catalytic hydrodehalogenation for organohalogenated micropollutants removal

The presence of organohalogenated micropollutants in drinking water represents an issue of increasing concern, and stringent regulations are being developed in this regard. As representative example, it must be noted that, apart from the well-known THMs, HAAs have been included in the recent Directive 2020/2184/EU, focused on the quality of water intended for human consumption. In addition to those contaminants, other organohalogenated compounds such as pesticides are also under regulation. Nevertheless, other emerging halogenated contaminants are still being investigated and are not regulated. Accordingly, the search for innovative treatments that warrant the effective elimination of such compounds is crucial.

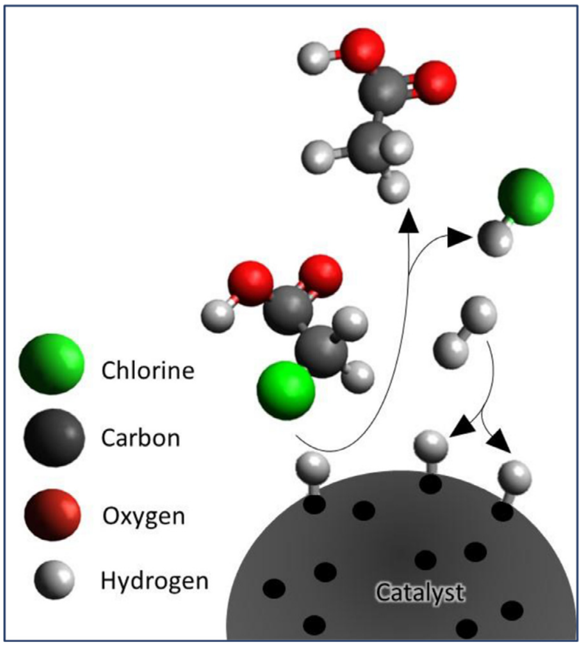


Fig. 2. MCAA catalytic hydrodehalogenation reaction scheme.

So far, advanced oxidation technologies such as Fenton-based processes, UV-light irradiation/H_2O_2 and ozonation have received major attention for the removal of organohalogenated compounds in the literature (Guzzella et al., 2002; Perez-Estrada et al., 2005; Poerschmann et al., 2009; Schmidt and Brauch, 2008). However, these processes usually require long reaction times to achieve the removal of short organic molecules like THMs or HAAs (Shemer and Narkis, 2005), and can also generate more toxic intermediates than the parent compounds (Munoz et al., 2011; Diaz et al., 2016; Pérez-Moya et al., 2007). In practice, adsorption onto activated carbon is the conventional process which shows the highest efficiency for the removal of emerging pollutants in DWTPs (Leone et al., 2018). Although it can remove organohalogenated compounds to a high extent, further treatments of the saturated adsorbent are required, which is not desirable from both economic and environmental points of view (Liu et al., 2016).

As has been abovementioned, the toxicity and persistence of organohalogenated pollutants is directly associated with the carbon-halogen bond. Consequently, catalytic hydrodehalogenation (HDH) appears as a promising alternative to eliminate organohalogenated micropollutants. In this process, hydrogen reacts with the organohalogenated compound in the presence of a catalyst (usually based on precious metals as active phase) and the carbon-halogen bond is broken resulting in the replacement of the halogen by a hydrogen atom. Thus, hydrogenated halogen-free products and the corresponding hydrohalic acids are obtained (Mackenzie et al., 2006). This transformation commonly leads to a notable abatement of the effluent toxicity (Keane, 2011). As example, Fig. 2 shows the scheme of the HDH reaction of MCAA.

The general equation of the HDH reaction can be expressed as follows:

$$C_xH_yX_z + zH_2 \rightarrow C_xH_{y+z} + zHX$$

One of the main advantages of HDH is that it allows operating under ambient conditions within a wide range of initial pollutant concentrations. Accordingly, most HDH studies have been carried out under ambient conditions (temperature and pressure). The application of more severe operating conditions has been mainly evaluated for the treatment of highly polluted industrial wastewaters (Calvo et al., 2007;

Nangoi et al., 2010). For instance, Calvo et al. (2007) carried out the treatment of kraft pulp industry effluents by HDH operating at a temperature range from 25 to 100 °C and pressure from 1 to 11 bar. Regarding the reductant agent, molecular hydrogen has been commonly employed by bubbling gaseous hydrogen into the reaction medium (Kopinke et al., 2004; Mackenzie et al., 2006). The main advantage is to avoid the formation of waste products. The use of alternative sources of reductants has been also investigated, mainly for the treatment of highly polluted wastewaters where the feed of H_2 could be insufficient due to its low solubility (0.84 mM at 15 °C and 100 kPa). Formic acid and, to a lower extent, hydrazine, have been mainly evaluated (Kopinke et al., 2004; Wang et al., 2010; Yu et al., 2016). For instance, Yu et al. (2016) investigated the removal of trichloroethylene (TCE) in water using formic acid, obtaining ethane and HCl as reaction products. Moreover, Miyabe et al. (2003) studied TCE hydrodechlorination using hydrazine as reductant, showing that the process efficiency was highly influenced by pH conditions. All in all, these alternative sources of hydrogen present important shortcomings such as poisoning of the active sites of the catalysts or metal leaching by using acid solutions. Therefore, the use of hydrogen gas is a clean solution and the most suitable for the treatment of organohalogenated micropollutants in DWTPs. Due to the low concentration of the micropollutants, H_2 bubbling would be enough, despite its low solubility, and additional water residues would be avoided.

So far, HDH has been mainly explored for the removal of organohalogenated pollutants in industrial wastewaters such as those coming from the production of pesticides or paper (Nangoi et al., 2010; Yuan and Keane, 2003). Nevertheless, more recently, this technology has been also evaluated for the removal of organohalogenated micropollutants that can affect drinking waters. Table 2 summarizes the literature works dealing with the application of HDH for such type of target pollutants. As can be observed, this technology has proved to be highly effective for the complete removal in short reaction times under ambient conditions of a wide range of compounds such as pharmaceuticals, pesticides, personal care products and DBPs. In the following sub-sections, the choice of catalyst and the role of the micropollutants nature on the performance of the process will be deeply evaluated. Catalyst deactivation phenomena will be also addressed and a review on the most effective regeneration procedures developed so far will be offered. Finally, the integration of the HDC technology in the DWTP scheme will be analyzed, and the scaling-up of the process will be addressed.

3.1. The choice of catalyst

HDH catalysts commonly consist of a precious metal homogeneously dispersed onto a material of high specific surface area that acts as support. The latter must guarantee an adequate interaction and dispersion of the metal to increase the number of available active sites as well as to warrant their stability. These active sites, specially, the electron-deficient species of the metal, are the responsible for hydrogen molecule adsorption and dissociation, while the zero-valent ones are the responsible for halogenated compounds adsorption, leading to the carbon-chlorine bond breakdown. The choice of appropriate supports is crucial to stabilize metal particles and avoid particle aggregation (Zheng et al., 2020). Furthermore, they can also influence the reagents adsorption and mass transfer processes (Lan et al., 2019). The most used supports in the HDH system are alumina (Al_2O_3), activated carbon (AC), silicon oxide (SiO_2), cerium oxide (CeO_2) and zirconia (ZrO_2) (Lowry and Reinhard, 2000; Mackenzie et al., 2006; Nieto-Sandoval et al., 2018).

The use of inert materials as supports has proved to be especially advantageous compared to carbonaceous solids. As representative example, it must be mentioned the study of Yuan and Keane (2004), who evaluated the effect of the support in the HDH of chlorophenols using Pd/Al_2O_3 and Pd/AC catalysts. Although both catalysts were highly active, Pd/Al_2O_3 showed a substantially higher stability after sequential uses, showing a performance close to that of the fresh catalyst, while the reuse of Pd/AC catalyst was accompanied by a notable loss of activity. The deactivation of this catalyst was explained by a substantial decrease in the specific surface area (up to 60%) due to the adsorption of reaction species as well as by a remarkable Pd leaching (*ca.* 40%) caused by the corrosive action of HCl (Yuan and Keane, 2004). It was then demonstrated that significantly stronger metal/support interactions prevalent in Pd/Al_2O_3 compared to Pd/AC, and that the lower adsorption capacity of the former prevents its fouling to a high extent. In a more recent work, Wu et al. (2015) evaluated the role of the catalytic support in the HDH of DCF using Pd-supported onto different materials such as Al_2O_3, AC, SiO_2 and CeO_2. Again, an inert material was selected as prominent support. Pd/CeO_2 was found to be the optimum catalyst followed by Pd/Al_2O_3 in terms of activity. Nevertheless, Pd/CeO_2 showed a significant progressive deactivation after consecutive applications (Wu et al., 2015). In this sense, Zheng et al. (2020) obtained similar results during the hydrodehalogenation of the undesired disinfection by-product bromochloroacetic acid using palladium-based catalysts, concluding that the supports with the highest PZC values gave rise to stronger electro-static attraction between the reactant and the catalysts surface and showed higher catalytic activity. In more recent works (Nieto-Sandoval et al., 2018, 2019a, 2019b, 2020a, 2020b), the high activity and remarkable stability of Pd/Al_2O_3 have been newly demonstrated, being this catalyst recognized as one of the most suitable in this field. In fact, its successful application for the removal of a wide range of organohalogenated micropollutants such as pharmaceuticals, pesticides, personal care products and DBPs has been already demonstrated and will be discussed in detail in the following section.

Regarding the active phase, precious metals such as Pd, Rh or Pt have been commonly used due to their high capacity for the hydrogenolysis of C-X bonds (Arias and Correa, 2007; Diaz et al., 2009; Diaz et al., 2016; Munoz et al., 2014). Among them, Rh and Pd have shown the highest activity in HDH reactions, obtaining kinetic constants in the removal of chlorophenols of 1.41 and 2.68 $L\ min^{-1}\ g_{metal}^{-1}$, respectively, compared to Pt catalysts (0.17 $L\ min^{-1}\ g_{metal}^{-1}$) which, also, have showed a progressive deactivation due to the adsorption of chlorinated species for the treatment of chlorophenols (Molina et al., 2014). Furthermore, the HDH of the flame retardant tetrabromobisphenol A (TBBPA) with Pd, Pt and Rh catalysts have been recently investigated (Nieto-Sandoval et al., 2021a). Although TBBPA sharply decreased in all cases, obtaining a kinetic constant of 0.88 $L\ min^{-1}\ g_{cat}^{-1}$ using the Pd catalyst, the debromination stage took considerably longer times using Pt and Rh catalysts. In fact, after 2 h of reaction bromine balance was not closed with these catalysts, while with the Pd/Al_2O_3 catalyst it was closed in 5 min. Although in other cases Rh catalysts have been very active for hydrodehalogenation, showing also high activity for the hydrogenation step (Diaz et al., 2008), Pd catalysts are the most widespread used due to their high activity under ambient conditions for a wide variety of organohalogenated compounds and their high resistance to HCl poisoning (Diaz et al., 2015; Munoz et al., 2014). Hydrodehalogenation reaction is strongly influenced both by the size and the oxidation state of the precious metal which constitutes the active sites of the catalyst. Accordingly, increasing the metal dispersion, which results in a decrease in particle size, leads to a greater number of accessible active sites allowing to minimize the amount of active phase required to catalyze a specific reaction and thus, to reduce the catalyst cost. Fig. 3 shows Pd nanoparticles by TEM image and zerovalent (Pd^0) and electrodeficient (Pd^{n+}) palladium bands obtained from the XPS analysis of a commercial Pd/Al_2O_3 catalyst. The presence of both palladium species (zerovalent and electrodeficient) in the catalyst surface is necessary to obtain active palladium-based catalysts in HDH reactions since they are responsible of hydrogen and halogenated compounds chemisorption, respectively. The surface Pd^{n+}/Pd^0 molar ratio calculated from the XPS analysis of Pd/Al_2O_3 catalyst was 1.04, close to 1 which is the optimal value proposed by Gomez-Sainero et al. (2002) for the aforementioned catalysts during HDH reactions. In addition, bimetallic catalysts are receiving special attention. The combination of various noble metals can increase the

Table 2
Summary of the application of HDH for organohalogenated micropollutants removal.

Catalyst	Target pollutant	Operating conditions	Water matrix	Results	Stability	Reference
Bio-Pd/Au	Diclofenac (DCF)	C_{DCF} = 20 mg L^{-1} C_{cat} = 50 $mg_{Pd/Au}$ L^{-1} T = 25 °C pH = 7 H_2	Deionized water	X_{DCF} = 78% (24 h)	Not studied	(De Corte et al., 2011)
Bio-Pd/Au	Diclofenac (DCF)	C_{DCF} = 20 mg L^{-1} C_{cat}=50 $mg_{Pd/Au}$ L^{-1} T = 25 °C pH = 7 H_2	Deionized water and hospital WWTP effluent	X_{DCF} = 43% (24 h in WWTP effluent)	Not studied	(De Corte et al., 2012)
Pd/ZrO_2 (1.74% wt.)	Monochloroacetic acid (MCAA) Dichloroacetic acid (DCAA) Trichloroacetic acid (TCAA)	C_{cont} = 0.16 mmol L^{-1} C_{cat} = 0.15 g L^{-1} T = 25 °C pH = 5.6 H_2 = 250 mL min^{-1}	Deionized water	X_{cont} = 100% (120 min)	Not studied	(Zhou et al., 2013)
Pd/CeO_2 (2.6% wt.)	Diclofenac (DCF)	C_{cont} = 0.24 mmol L^{-1} C_{cat} = 0.1 g L^{-1} T = 25 °C pH = 9 H_2 = 250 mL min^{-1}	Deionized water	X_{DCF} = 100% (60 min)	After 5 runs, activity decreased 75%	(Wu et al., 2015)
Au–Pd bimetallic nanoparticles	Chloramphenicol (CAP)	C_{cont} = 50 mg L^{-1} C_{cat} = 10 g L^{-1} T = 25 °C pH = 7 H_2	Deionized water	X_{DCF} = 100% (3 h)	After 3 runs, constant activity X_{DCF} = 99%	(Wang et al., 2015a; Wang et al., 2015b)
Resin supported Pd catalyst (2% wt.)	Triclosan (TCL)	C_{cont} = 2.9 mg L^{-1} Resin = 1 g L^{-1} T = 20 °C pH = 4.9	Deionized water and 10 mM NaCl matrix	X_{TCL} = 100% (120 min)	After 8 runs, K_{obs} = 1.24 L g^{-1} min^{-1}	(Han et al., 2017)
Pd/Al_2O_3 (1% wt.)	Diclofenac (DCF)	C_{DCF} = 0.068 mmol L^{-1} C_{cat} = 0.5 g L^{-1} T = 25 °C pH = 7 H_2 = 50 mL min^{-1}	Deionized water WWTP effluent Surface water	X_{DCF} = 100% (30 min)	After 3 runs, constant activity X_{DCF} = 100% (30 min)	(Nieto-Sandoval et al., 2018)
Pd/Al_2O_3 (1% wt.)	Diclofenac (DCF) Triclosan (TCL) Sertraline (SRT) Chloramphenicol (CAP) Trichloromethane (TCM)	C_{cont} = 3 mg L^{-1} C_{cat} = 0.25 g L^{-1} T = 25 °C pH = 7 H_2 = 50 mL min^{-1}	Deionized water Mineral water Tap water Surface water	X_{cont} = 100% (60 min) X_{TCM} = 100% (30 min, C_{TCM} = 100 µg L^{-1}, C_{cat} = 1 g L^{-1})	After 5 runs, constant activity X_{cont} = 100% (60 min)	(Nieto-Sandoval et al., 2019b)
Pd/Al_2O_3 (1% wt.)	Chlorpromazine (CPZ)	C_{CPZ} = mg L^{-1} C_{cat} = 0.25 g L^{-1} T = 25 °C pH = 7 H_2 = 50 mL min^{-1}	Deionized water	X_{CPZ} = 100% (90 min)	After 5 runs, activity decreased 100%	(Nieto-Sandoval et al., 2019a)
Pd/CeO_2 (1.4% wt.)	Monochloroacetic acid (MCAA) Bromochloroacetic acid (BCAA)	C_{cont} = 0.2 mmol L^{-1} C_{cat} = 0.05 g L^{-1} T = 25 °C pH =5.6 H_2 = 100 mL min^{-1}	Deionized water	X_{cont} = 100% (30 min)	After 5 runs, activity decreased 34%	(Zheng et al., 2020)
Pd/Al_2O_3 (1% wt.)	Monochloroacetic acid (MCAA) Dichloroacetic acid (DCAA) Trichloroacetic acid (TCAA) Monobromoacetic acid (MBAA) Dibromoacetic acid (DBAA) Bromochloroacetic acid (BCAA)	C_{cont} = 0.05 mmol L^{-1} C_{cat} = 0.50 g L^{-1} T = 25 °C pH =7 H_2 = 50 mL min^{-1}	Deionized water	X_{cont} = 100% (60 min)	Not studied	(Nieto-Sandoval et al., 2020a)
Pd/Al_2O_3 (1% wt.)	Acetamiprid (ACT) Imidacloprid (IMD) Clothianidin (CLT) Thiacloprid (THC) Thiamethoxam (THX)	C_{cont} = 1 mg L^{-1} C_{cat} = 0.25 g L^{-1} T = 25 °C pH =7 H_2 = 50 mL min^{-1}	Deionized water	X_{cont} = 100%, except X_{THC} = 80% (30 min)	After 4 runs, $X_{ACT\text{-}IMD}$ = 100% X_{CLT} = 45% X_{THC} = 5% X_{THX} = 73% (15 min)	(Nieto-Sandoval et al., 2020b)

activity towards HDH process. In this sense, Wang et al. (2015a) developed Au–Pd bimetallic nanoparticles for the hydrodechlorination of DCF showing that the combination of both metals resulted in 95% conversion, while the use of them individually lead to negligible or much lower activity. Although Au metal present low capacity to adsorb hydrogen, Au can activate C-Cl bond that is subsequent attacked by hydrogen dissociated at the centers of other metal combined, increasing the activity. Nevertheless, the use of noble metals significantly increases the cost of the system. In this context, although transition metals are not active under ambient conditions, the combination of transition metals such as Fe or Ni with precious metals can accordingly reduce the catalyst cost (Wu et al., 2005). Munoz et al. (2016) studied PtNi catalysts for HDC of 4-chlorophenol, showing low activity of monometallic Ni catalyst and a progressive deactivation of monometallic Pt catalyst due to chlorine

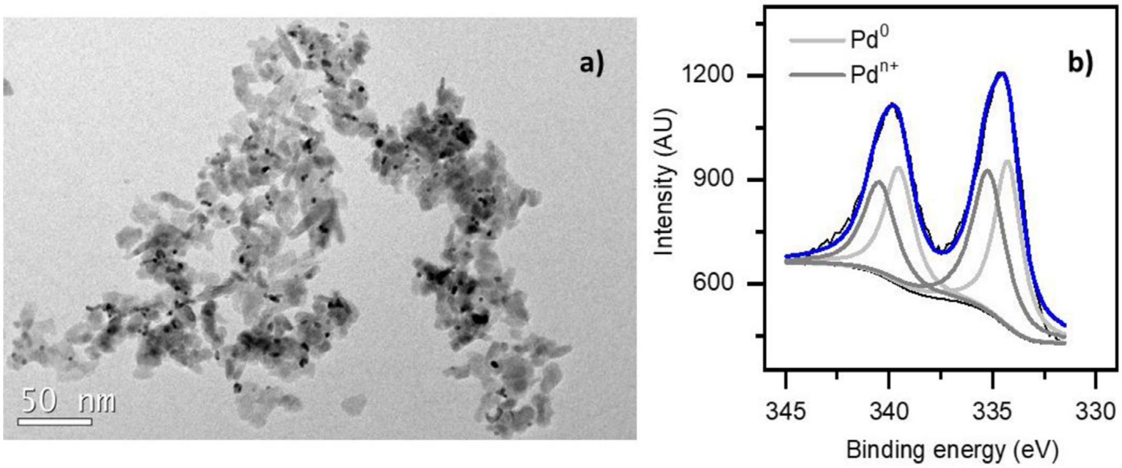


Fig. 3. Pd/Al_2O_3 catalyst: a) TEM image and b) deconvolution of the Pd 3d core-level spectra.

poisoning, while PtNi nanoparticles were notably active and stable after successive runs. In other work, a bimetallic Pd-Fe catalyst was developed for the treatment of 4-chlorophenol, remaining the activity and obtaining a magnetic catalyst which is useful for further separation. However, up to 10% of iron leaching was observed after 3 h experiment, which is an important drawback for water treatment (Munoz et al., 2014). Therefore, although bimetallic catalysts with transition metals allow to reduce the catalyst cost, taking advantage of the precious metal properties (Golubina et al., 2006; Zhou et al., 2010), their limitations with regard catalyst stability and metal leaching hinder their use in water treatment (Calvo et al., 2008). Further investigation should be conducted in this field.

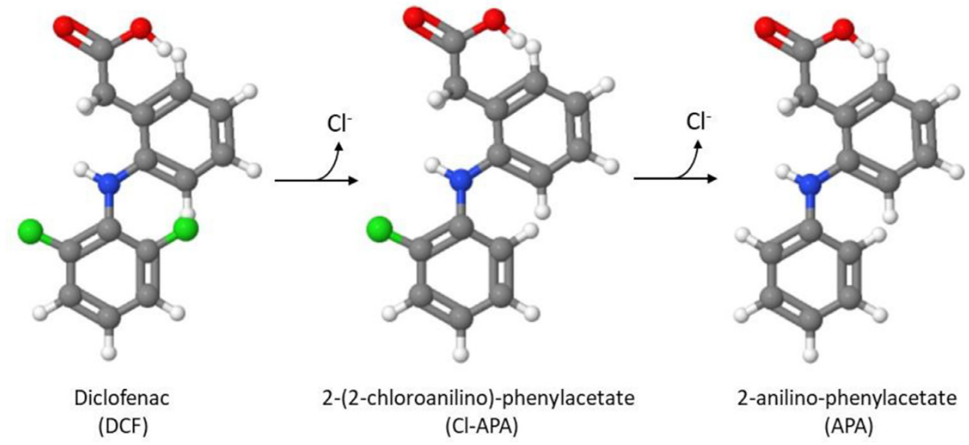
3.2. Role of organohalogenated micropollutants nature on HDH. Impact on activity and stability

The nature of the organohalogenated compounds as well as the kind and number of halogen substituents can play an important role in their reactivity towards HDH. As previously mentioned, HDH has been applied for the dehalogenation of different micropollutant families such as pharmaceuticals, pesticides, personal care products and DBPs. For the sake of comparison, the kinetic constants obtained in the HDH of representative groups of these pollutants using a commercial Pd/Al_2O_3 catalyst at 25 °C in deionized water are collected (see Table S1 of Supporting Information) (Nieto-Sandoval et al., 2019a, 2019b, 2020a, 2020b). The process allowed to achieve the complete removal of all these compounds in relatively short reaction times (<60 min), obtaining kinetic constant values in the range of 0.12– L $g^{-1}{}_{cat}$ min^{-1}. Although no significant differences can be found among the groups of organohalogenated pollutants evaluated, there are specific compounds in all these groups that showed a significantly higher reactivity towards HDH. The reasons behind such differences in the reactivity of the pollutants will be discussed below by analyzing the results obtained in each of these families.

Pharmaceutical compounds have been devoted to HDH treatment in a number of works (De Corte et al., 2011, 2012; Nieto-Sandoval et al., 2018, 2019b; Wu et al., 2015). These compounds present complex structures formed by aromatic rings and groups such as nitro, amide, alcohols, sulfur and, as previously mentioned, halogens substituents. The anti-inflammatory drug diclofenac (DCF) has been highly investigated given its high persistence and ubiquitous occurrence in natural waters (De Corte et al., 2011, 2012; Nieto-Sandoval et al., 2018; Wu et al., 2015). Moreover, other pharmaceuticals, such as the antidepressant sertraline (SRT) and the antibiotic chloramphenicol (CAP), as well as the antibacterial agent triclosan (TCL) have been completely removed by HDH reaction. In this case, the reactivity towards HDH could be explained by the number of available positions where the nucleophilic substitution by hydrogen can take place (Nieto-Sandoval et al., 2019b). According to the obtained kinetic constants in the range of 0.32–1.56 L $g^{-1}{}_{cat}$ min^{-1}, the reactivity increased in the following order: SRT<DCF<TCL<CAP. Remarkably, CAP showed four available positions (two chlorine atoms, a nitro and an amide groups), TCL present three chlorine atoms and DCF and SRT, two chlorine atoms. Furthermore, the molecule pKa value plays a particular role in the reactivity towards HDH due to its influence in the attraction between the charges of the molecule and the catalyst surface. In this case, since the experiments were carried out at natural pH and during reaction this value decreased due to the HCl production, the surface of the Pd/Al_2O_3 catalyst was positively charged (pH_{PZC}=8.7). Therefore, SRT suffered an electrostatic repulsion due to its high pKa value (9.16). Moreover, although the antipsychotic CPZ was completely removed by HDH, particularly the presence of sulfur in its structure led to a progressive catalyst deactivation due to the strong interaction between sulfur and Pd active sites.

Pesticides have been also widely subjected to HDH treatment. Pesticides present complex structures and mostly with aromatic rings, sometimes more than one. Remarkably, they usually contain a high number of halogen substituents. As pharmaceuticals, their reactivity towards HDH could be explained by the positions susceptible of substitution by hydrogen but they have shown some differences. Several works have dealt with chlorophenols removal by HDH achieving complete conversion (Calvo et al., 2010; Diaz et al., 2016; Mendes et al., 2021). However, the reactivity towards HDH decreased with the number of chlorine substituents, attributed to a higher stability of C-Cl bonds (Xia et al., 2009; Zhou et al., 2010). More recently, the dehalogenation of five neonicotinoid pesticides listed in the EU Watch List (Decision 2018/840) has been evaluated through HDH. This work was focused on the effect of micropollutant nature on the activity and stability of a Pd/Al_2O_3 catalyst. Both pesticides, ACT and IMD, with one chlorine atom showed similar kinetic constants (2 L $g^{-1}{}_{cat}$ min^{-1}). However, sulfur-bearing structures led to a progressive catalyst deactivation due to the catalyst poisoning (Nieto-Sandoval et al., 2019a, 2020). Remarkably, it should be noted that sulfur-free compounds were disfavored when the five micropollutants were treated in a mixture, confirming that the interaction of sulfur-containing pollutants with Pd active sites is significantly favored.

A huge range of DBPs have been completely removed by HDH technology, specially the most common trihalomethanes and haloacetic acids. These compounds are characterized by a simple molecular structure, without aromatic rings, but usually present bromine and chlorine substituents. As it has been aforementioned, the number and kind



Scheme 1. Reaction pathway for the HDH of DCF using Pd/Al_2O_3 catalyst.

of halogen substituents influence the reactivity towards HDH of the organohalogenated compounds. Thus, bromoacetic acids have shown higher reactivity than the chlorinated ones, which was attributed to the lower C-Br bond dissociation energy. As shown in Table S1 (see Supporting Information), the kinetic constants obtained for MCAA and MBAA were 0.12 and 1.25 L g_{cat}^{-1} min^{-1}, respectively. In addition, in the case of chloroacetic acids, the reactivity increased with the halogenation degree, specially from one to two chlorine atoms. Nevertheless, this trend was not followed by the brominated ones since similar kinetic constants were obtained regardless of the bromine content (Nieto-Sandoval et al., 2020a). Moreover, trihalomethane was completely removed in 30 min, obtaining a kinetic constant of 0.28 L g_{cat}^{-1} min^{-1} (Nieto-Sandoval et al., 2019b). Similar results regarding the chlorination degree were reported by Mackenzie et al. (2006) for chloromethanes HDH, obtaining higher Pd/Al_2O_3 catalyst activity for tetrachloromethane than trichloromethane, corresponding to C-Cl bond strengths of 306 and 339 kJ mol^{-1}, respectively.

So far, the reaction pathways of HDH process for organohalogenated micropollutants removal have been evaluated via stepwise, following a consecutive dehalogenation reaction, and/or concerted reactions, where simultaneous dehalogenation of more than one halogen takes place (Nieto-Sandoval et al., 2019b; Zheng et al., 2020; Zhou et al., 2013). For instance, the removal of DCF by HDH followed a consecutive reaction pathway (see Scheme 1), obtaining the chlorine-free hydrogenated 2-anilinophenylacetate (APA) as final product (Nieto-Sandoval et al., 2018). Furthermore, it has been demonstrated that concerted reactions gained importance with increasing the chlorination degree (Nieto-Sandoval et al., 2020a).

All in all, it must be highlighted that HDH technology allows to significantly decrease the toxicity of the effluent regardless of the nature of the organohalogenated pollutant treated, due to the generation of halogen-free hydrogenated products. For instance, the antibacterial agent triclosan, characterized by a high toxicity, was completely removed by HDH, reaching negligible ecotoxicity values in 10 min reaction time (Han et al., 2017; Nieto-Sandoval et al., 2019b). In the same way, the pharmaceuticals DCF, CAP, SRT and CPZ with EC_{50} values of 6.2, 404, 8.8 and 3.3 mg L^{-1}, respectively, were treated by HDH leading to nontoxic effluents (Nieto-Sandoval et al., 2019a, 2019b). Wu et al. (2015) also evaluated the treated DCF effluent after HDH on *Daphnia magna* showing that the 48 h-EC_{50} value of a diclofenac solution increased from 21.5% (in% dilution) to 35.1% when DCF was completely dechlorinated. This is a notable benefit of HDH technology in comparison with other treatments such as oxidation processes that can lead to more toxic compounds. For instance, Zhao et al. (2009) evaluated the toxicity by *Vibrio fischeri* along an electro-oxidation reaction of DCF resulting that the inhibition increase up to 89% in 2 h reaction showing that transformation intermediates were more toxic than single diclofenac (65%).

3.3. Development of effective catalyst regeneration procedures

Given the high cost of the catalysts used, one of the main limitations of the HDH system is catalyst deactivation. It can be attributed to multiple phenomena such as poisoning of the metal active sites by hydrohalic acids formed along reaction, leaching of the metal or byproducts adsorption and fouling (Ordóñez et al., 2007). Although the application of HDH in DWTPs would imply the treatment of highly diluted streams, where catalyst deactivation would be less favored, it is crucial to evaluate such phenomenon. Understanding the reasons behind catalyst deactivation would also allow to develop effective regeneration procedures and thus, to facilitate the potential application of this technology in DWTPs.

The release of HCl or HBr along reaction, immediately dissociated in liquid phase, leads to the acidification of the reaction medium and can also affect the catalyst surface. This is, in fact, one of the main causes of catalyst deactivation in HDH, which limits the process and increases the costs (Yuan and Keane, 2003). Furthermore, metal leaching can pose a risk from the environmental point of view (Egorova and Ananikov, 2016). Operating under slightly alkaline conditions by the addition of different bases like NaOH or KOH has proved to prevent this kind of catalyst poisoning (de Pedro et al., 2011). Moreover, in order to achieve a more stable anchorage of the active phase onto the support and reduce metal leaching, an oxidative treatment with nitric acid have showed promising results in a Pd on activated carbon catalyst (Calvo et al., 2010). Nevertheless, considering that micropollutants would appear at very low concentrations in DWTPs, the generation of halide species would not remarkably affect the stability of the catalyst. Furthermore, Pd/Al_2O_3 catalyst would be preferentially used and, as has been previously explained, it showed a strong Pd-support interaction.

The outstanding stability of Pd/Al_2O_3 in the HDH of a wide range of micropollutants (pharmaceuticals, pesticides, personal care products and DBPs) has been recently demonstrated (Nieto-Sandoval et al., 2019a, 2019b, 2020a, 2020b). Nevertheless, it must be noted that sulfur-bearing pollutants such as the neonicotinoid pesticides (CLT, THC and THM) or the pharmaceutical chlorpromazine led to a progressive deactivation of the catalyst after consecutive HDH runs (Nieto-Sandoval et al., 2019a, 2020b). This fact was attributed to the selective interaction of sulfur species on Pd surface resulting in a blocking of active sites.

The water matrix composition can also affect the stability (and activity) of the catalyst since the presence of co-existing substances like salts or organic content can lead to its poisoning and/or fouling. The occurrence of such species could have a major impact on the catalytic performance when they appear at relatively high concentrations. For instance, Heck et al. (2009) found a 70% activity decrease in the presence of chloride (0.02 M NaCl) and sulfide ($S:Pd_{surf}$ ratio up to 1) ions due to catalyst poisoning by Cl and S atoms chemisorption onto Pd active sites. In a more recent work, the HDH of DCF in hospital wastewater exhibited a prominent inhibition due to poisoning of the active sites by the presence of salts (Nieto-Sandoval et al., 2018). Nevertheless, the matrix effect on the performance of Pd/Al_2O_3 has been of negligible importance when water matrices of characteristics more similar to the ones found in DWTPs have been tested (Nieto-Sandoval et al., 2019b). For instance, HDH was successfully applied for the removal of DCF, TCL, CAP and SRT pharmaceuticals in different real water matrices (mineral water, tap water and surface water). The conductivity values of these matrices were in the range from 41 to 200 $\mu S\ cm^{-1}$. The other parameters analyzed were chloride ions (0.35–14.1 $mg\ L^{-1}$), organic carbon (0.3–2.7 $mg\ L^{-1}$) and inorganic carbon (3.5–14.9 $mg\ L^{-1}$). Far from any sign of deactivation, the catalyst led to HDH rates even slightly higher than those obtained in deionized water, which was attributed to the neutralization of the chloride ions generated along reaction by the presence of a moderate concentration of salts (Nieto-Sandoval et al., 2019b).

Neither the halides generated along reaction nor the water matrix composition represent any significant threat for the stability of the catalyst (Pd/Al_2O_3) in the potential application of HDH in DWTPs. Nevertheless, as has been previously mentioned, the presence of sulfur-bearing micropollutants could lead to a progressive deactivation of the catalyst. Accordingly, the development of catalyst regeneration procedures should be developed to warrant its reusability. These processes must ensure the complete restoration of the catalyst activity while maintaining its outstanding properties. In this sense, the main issues that should be considered are the possible sintering of Pd nanoparticles as well as Pd leaching and/or metal oxidation.

As shown in Table 3, which summarizes the main methods applied for catalyst regeneration in HDH processes, both thermal and chemical treatments have been investigated. Regarding thermal treatments, it must be noted that the unique application of calcination did not allow to restore the activity of Pd/Al_2O_3 due to the oxidation of the Pd active sites. In fact, the Pd^0/Pd^{n+} ratio was decreased from 1.01 to 0.47 (Nieto-Sandoval et al., 2019a). A consecutive reduction treatment after calcination allowed to recover almost completely the fresh catalyst activity, which confirmed the importance of keeping the Pd^0/Pd^{n+} ratio at around 1.

Although the consecutive calcination-reduction treatment has proved to be effective for the regeneration of the catalyst activity, it implies a high energy consumption. Accordingly, the search for more cost-effective and environmentally friendly alternatives is receiving increasing attention. Chemical oxidative methods have been mainly explored in this regard. They are based on the washing of the catalyst by different solutions such as NaOH, $KMNO_4$, H_2O_2 or NaClO (see Table 3). The application of $KMNO_4$ was not effective for Pd/Al_2O_3 regeneration because it led to a strong oxidation of metal species ($Pd^0/Pd^{n+} = 0.3$). On the other hand, both H_2O_2 and NaClO diluted aqueous solutions allowed to recover the initial activity of the Pd/Al_2O_3 catalyst. Nevertheless, only NaClO achieved the complete regeneration without modifying the oxidation state of the Pd active sites. This regeneration procedure is particularly promising given its fast mode of action, simplicity and low-cost. In fact, its effectiveness has been already demonstrated in consecutive HDC-regeneration runs in the treatment of pharmaceuticals and pesticides (Nieto-Sandoval et al., 2019a, 2020b).

3.4. Integration of catalytic hydrodehalogenation in DWTP scheme

The integration of HDH technology in DWTPs must ensure the effective removal of organohalogenated micropollutants in short reaction times while not negatively affecting the other treatment steps commonly employed in these plants (Fig. 1). On the other hand, it must be considered that DBPs are generated along the pre-oxidation treatment and thus, HDH should be positioned afterwards. Furthermore, the presence of organic matter could be counterproductive for the HDH performance. For instance, Han et al. (2017) reported that the presence of humic acid at 30 $mg\ L^{-1}$ of TOC decreased the reaction constant rate 27% for the removal of the antibacterial agent TCL. The occurrence of suspended solids could also lead to the fouling of the catalyst. Accordingly, HDH should be preferentially applied as a purification step.

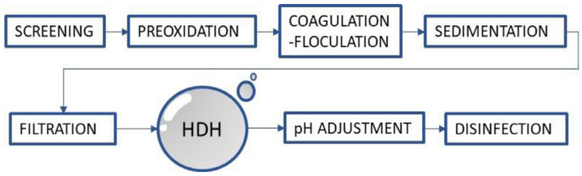


Fig. 4. Process diagram of the HDH system integration in a DWTP.

The final treatment applied in DWTPs is commonly disinfection, as it must ensure the biological quality of water along the whole distribution network. This process is usually carried out by the addition of monochloramines instead of chlorine due to their higher stability (Bond et al., 2011; Moradi et al., 2017). In a recent work, the effect of HDH on monochloramines from tap water (0.97 $mg_{Cl2}\ L^{-1}$) was evaluated, and their complete degradation was achieved in less than 30 min operating under ambient conditions (Nieto-Sandoval et al., 2019b). Even in the absence of catalyst, their concentration was reduced up to 70% by stripping. Based on these results, it is clear that the HDH treatment in a DWTP should be located prior the disinfection step to avoid the removal of the chloramines. On the other hand, since the generation of hydrohalic acids should be neutralized, the HDH treatment should be carried out before the pH adjustment. Fig. 4 shows a process diagram of the proposed integration of HDH in a conventional DWTP.

3.5. HDH process scaling-up

Catalytic hydrodehalogenation has been successfully tested at lab scale by conventional catalytic processing (*i.e.* slurry batch reactors) using powdered catalysts (see Table 1). The application of this technology at larger scales must consider long-term operation in continuous mode while keeping its high removal efficiency. For this configuration, the employment of powdered catalysts involves important shortcomings like difficult catalyst recovery and high pressure drops. Thus, its implementation at larger scale remains an important challenge that has been scarcely investigated. The used of fixed bed reactors packed with granular catalysts appears as an alternative for such goal, but large pressure drops and risk of blockage could be suffered (Avril et al., 2017; Koekemoer and Luckos, 2015). Xiong et al. (2018) evaluated chlorophenols HDH using a novel Pd/CNTs-Ni composite catalyst showing high efficiency and stability after 60 h, but the reaction was controlled by H_2 mass transfer limitations, which is an important drawback. Clearly, uniform flow and optimal mixing should be warranted in these systems (Müller et al., 2015). Accordingly, the development of structured catalysts would represent an important step forward. For instance, Luo et al. (2020) showed promising results with the development of a continuous system based on the deposition of Pd nanoparticles on H_2 transfer hollow fiber membranes for the dechlorination of 1,1,1-trichloroethane and TCE. High conversions were achieved and just 4% of Pd was lost over 90 days of continuous operation, overcoming one of the principles limitations (Luo et al., 2020). More recently, Nieto-Sandoval et al. (2021b) developed an innovative Pd-based Catalytic Membrane Reactor (CMR) which consists in a cylindrical inert porous alumina membrane as support decorated in the outer surface by Pd nanoparticles. In this system, hydrogen permeates through the porous material to the external membrane surface, where a controlled reaction zone is formed to favor the three-phase contact. The catalytic system was applied for the removal of the anti-inflammatory DCF with reasonable conversion, showing an extraordinary stability for up to 200 h.

4. Prospects and concluding remarks

This review summarizes the application of aqueous-phase catalytic hydrodehalogenation (HDH) as a promising alternative to deal with fur-

Table 3
Summary of regeneration methods applied in HDH processes.

Category	Regeneration method	Deactivation	Catalyst	Target pollutant	Operating conditions	Results	Reference
Thermal	Calcination 200 °C 3 h	Species adsorption fouling	Pd/AC	4-chloro-2-methylphenoxyacetic acid (MCPA)	$C_{MCPA} = 0.075$ mmol L^{-1}, 0.4 mL min^{-1} $C_{cat} = 2.75$ g L^{-1} $T = 30$ °C $H_2 = 50$ mL min^{-1}	Not effective	(Diaz et al., 2016)
	Calcination 200 °C 3 h-reduction 150 °C 2 h	Species adsorption fouling	Pd/AC	4-chloro-2-methylphenoxyacetic acid (MCPA)	$C_{MCPA} = 0.075$ mmol L^{-1}, 0.4 mL min^{-1} C_{cat}=2.75 g L^{-1} $T = 30$ °C $H_2 = 50$ mL min^{-1}	Not effective	(Diaz et al., 2016)
	calcination 250 °c 2 h	sulfur compounds	Pd/Al_2O_3 (1% wt.)	Chlorpromazine (CPZ)	$C_{CPZ} = 3$ mg L^{-1} $C_{cat} = 0.25$ g L^{-1} $T = 25$ °C pH =7 $H_2 = 50$ mL min^{-1}	$X_{CPZ} = 0\%$ (90 min)	(Nieto-Sandoval et al., 2019a)
	calcination 250 °c 2 h -reduction 150 °c 1 h	sulfur compounds	Pd/Al_2O_3 (1% wt.)	Chlorpromazine (CPZ)	$C_{CPZ} = 3$ mg L^{-1} $C_{cat} = 0.25$ g L^{-1} $T = 25$ °C pH =7 $H_2 = 50$ mL min^{-1}	$X_{CPZ} = 99\%$ (90 min)	(Nieto-Sandoval et al., 2019a)
Chemical	kmno$_4$ 0.09 mmol L^{-1} pH =3 60 min	sulfide	Pd/Al_2O_3 (1% wt.)	Chlorobenzene (MCB)	$C_{MBC} = 20$ mg L^{-1} $C_{cat} = 0.15$ g L^{-1} $T = 25$ °C pH =13 H_2	Activity recovery 100%	(Angeles-Wedler et al., 2009)
	NaOH 1–1.5 mM 5 mL min^{-1} 8 h, 30 °C	Species adsorption fouling	Pd/AC	4-chloro-2-methylphenoxyacetic acid (MCPA)	$C_{MCPA} = 0.075$ mmol L^{-1}, 0.4 mL min^{-1} $C_{cat} = 2.75$ g L^{-1} $T = 30$ °C $H_2 = 50$ mL min^{-1}	Activity partially recovered Not stable	(E. Diaz et al., 2016)
	kmno$_4$ 50 mg L^{-1} 2 h, 25 °c	sulfur compounds	Pd/Al_2O_3 (1% wt.)	Chlorpromazine (CPZ)	$C_{CPZ} = 3$ mg L^{-1} $C_{cat} = 0.25$ g L^{-1} $T = 25$ °C pH =7 $H_2 = 50$ mL min^{-1}	$X_{CPZ} = 0\%$ (90 min)	(Nieto-Sandoval et al., 2019a)
	naclo 750 mg L^{-1} 2 h, 25 °c	sulfur compounds	Pd/Al_2O_3 (1% wt.)	Chlorpromazine (CPZ)	$C_{CPZ} = 3$ mg L^{-1} $C_{cat} = 0.25$ g L^{-1} $T = 25$ °C pH =7 $H_2 = 50$ mL min^{-1}	$X_{CPZ} = 100\%$ (90 min)	(Nieto-Sandoval et al., 2019a)
	h$_2$o$_2$ 1000 mg L^{-1} 2 h, 25 °c	sulfur compounds	Pd/Al_2O_3 (1% wt.)	Chlorpromazine (CPZ)	$C_{CPZ} = 3$ mg L^{-1} C_{cat}=0.25 g L^{-1} $T = 25$ °C pH =7 $H_2 = 50$ mL min^{-1}	$X_{CPZ} = 90\%$ (90 min)	(Nieto-Sandoval et al., 2019a)
	naclo 750 mg L^{-1} 2 h, 25 °c	sulfur compounds	Pd/Al_2O_3 (1% wt.)	Acetamiprid (ACT) Imidacloprid (IMD) Clothianidin (CLT) Thiacloprid (THC) Thiamethoxam (THX)	$C_{cont} = 1$ mg L^{-1} $C_{cat} = 0.25$ g L^{-1} $T = 25$ °C pH =7 $H_2 = 50$ mL min^{-1}	$X_{Cont} = 100\%$ (15 min)	(Nieto-Sandoval et al., 2020b)

ther quality drinking water regulations related to organohalogenated micropollutants occurrence. To date, HDH process has been successfully applied at lab scale for the removal of a wide variety of compounds (pharmaceuticals, personal care products, pesticides or disinfection by-products), reducing significantly the effluent toxicity under ambient conditions. Nevertheless, the nature of such pollutants can significantly influence their reactivity towards HDH. Remarkably, increasing the halogenation grade or depending on the kind of halogen substituents, *i.e.* brominated pollutants, higher reaction rates can been obtained, while the presence of sulfur-containing species can lead to a progressive catalyst deactivation.

With regard to the employed catalysts in HDH, the noble metal Pd is usually used as active phase and alumina has been proved to be an excellent support. Although it has shown a reasonable stability, catalyst deactivation can occur due to the hydrohalic acids formed along reaction, which can lead to metal leaching and, overall, by-products adsorption. To overcome this limitation, different catalyst regeneration procedures have been developed, being the subtle washing of the catalyst with NaClO especially promising given its high effectiveness and low cost. On the other hand, the development of bimetallic catalysts with transition metals is being also investigated with the aim of increasing the stability of the catalyst as well as reducing its cost.

HDH has proved to be a versatile process, being effective in different real water matrices such as mineral, tap and surface waters. In any case, the integration of this technology in a DWTP is intended as polishing step once major organic matter has been removed and prior pH adjustment and disinfection. Its implementation at larger scales must consider operating in continuous mode for long-term operation. In this sense, the development of structured catalysts, mainly catalytic membrane reactors, appears as a promising solution. Pd/CMR has proved an outstanding activity and stability for micropollutants abatement for up to 200 h.

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.

CRediT authorship contribution statement

Julia Nieto-Sandoval: Writing – original draft, Investigation, Methodology, Visualization. **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.

Acknowledgments

This research has been supported by the Spanish MINECO thorough the project PID2019-105079RB-I00 and by the CM through the project P2018/EMT-4341. J. Nieto-Sandoval thanks the Spanish MINECO for the FPI Predoctoral Grant (BES-2017-081346). M. Munoz thanks the Spanish MINECO for the Ramón y Cajal Postdoctoral Contract (RYC-2016-20648).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2022.100047.

References

Abusallout, I., Rahman, S., Hua, G., 2017. Effect of temperature and pH on dehalogenation of total organic chlorine, bromine and iodine in drinking water. Chemosphere 187, 11–18. doi:10.1016/j.chemosphere.2017.07.149.

Angeles-Wedler, D., Mackenzie, K., Kopinke, F., 2009. Sulphide-induced deactivation of Pd/Al_2O_3 as hydrodechlorination catalyst and its oxidative regeneration with permanganate. Appl. Catal. B Environ. 90, 613–617. doi:10.1016/j.apcatb.2009.04.023.

Arias, A.N., Correa, C., 2007. A review of liquid-phase catalytic hydrodechlorination. Ing. Investig. 27, 52–64.

Avril, A., Hornung, C.H., Urban, A., Fraser, D., Horne, M., Veder, J., et al., 2017. Continuous flow hydrogenations using novel catalytic static mixers inside a tubular reactor. React. Chem. Eng. 2, 180–188. doi:10.1039/C6RE00188B.

Bayen, S., Obbard, J.P., Thomas, G.O., 2006. Chlorinated paraffins: a review of analysis and environmental occurrence. Environ. Int. 32, 915–929. doi:10.1016/j.envint.2006.05.009.

Benner, J., Helbling, D.E., Kohler, H., Wittebol, J., Brezina, E., Prasse, C., et al., 2013. Is biological treatment a viable alternative for micropollutant removal in drinking water treatment processes? Water Res. 47, 5955–5976. doi:10.1016/j.watres.2013.07.015.

Bond, T., Huang, J., Templeton, M.R., Graham, N., 2011. Occurrence and control of nitrogenous disinfection by-products in drinking water–A review. Water Res. 45, 4341–4354. doi:10.1016/j.watres.2011.05.034.

Calvo, L., Gilarranz, M.A., Casas, J.A., Mohedano, A.F., Rodriguez, J.J., 2010. Hydrodechlorination of diuron in aqueous solution with Pd, Cu and Ni on activated carbon catalysts. Chem. Eng. J. 163, 212–218. doi:10.1016/j.cej.2010.07.034.

Calvo, L., Gilarranz, M.A., Casas, J.A., Mohedano, A.F., Rodríguez, J.J., 2007. Detoxification of kraft pulp ECF bleaching effluents by catalytic hydrotreatment. Water Res. 41, 915–923. doi:10.1016/j.watres.2006.11.018.

Calvo, L., Gilarranz, M.A., Casas, J.A., Mohedano, A.F., Rodríguez, J.J., 2008. Hydrodechlorination of alachlor in water using Pd, Ni and Cu catalysts supported on activated carbon. Appl. Catal. B Environ. 78, 259–266. doi:10.1016/j.apcatb.2007.09.028.

Carmona, E., Andreu, V., Picó, Y., 2014. Occurrence of acidic pharmaceuticals and personal care products in turia river basin: from waste to drinking water. Sci. Total Environ. 484, 53–63. doi:10.1016/j.scitotenv.2014.02.085.

Carro, N., Cobas, J., García, I., Ignacio, M., Mouteira, A., 2014. Distribution and trend of organochlorine pesticides in Galicia coast using mussels as bioindicator organisms. possible relationship to biological parameters. Chemosphere 102, 37–47 S0045-6535(13)01672-X [pii].

Christman, R.F., Norwood, D.L., Millington, D.S., Johnson, J.D., Stevens, A.A., 1983. Identity and yields of major halogenated products of aquatic fulvic acid chlorination. Environ. Sci. Technol. 17, 625–628. doi:10.1021/es00116a012.

Cizmas, L., Sharma, V.K., Gray, C.M., McDonald, T.J., 2015. Pharmaceuticals and personal care products in waters: occurrence, toxicity, and risk. Environ. Chem. Lett. 13, 381–394. doi:10.1007/s10311-015-0524-4.

Cordner, A., De La Rosa, V.Y., Schaider, L.A., Rudel, R.A., Richter, L., Brown, P., 2019. Guideline levels for PFOA and PFOS in drinking water: the role of scientific uncertainty, risk assessment decisions, and social factors. J. Expo. Sci. Environ. Epidemiol. 29, 157–171. doi:10.1038/s41370-018-0099-9.

Cristale, J., García Vázquez, A., Barata, C., Lacorte, S., 2013. Priority and emerging flame retardants in rivers: occurrence in water and sediment, daphnia magna toxicity and risk assessment. Environ. Int. 59, 232–243. doi:10.1016/j.envint.2013.06.011.

De Corte, S., Hennebel, T., Fitts, J.P., Sabbe, T., Bliznuk, V., Verschuere, S., et al., 2011. Biosupported bimetallic Pd-Au nanocatalysts for dechlorination of environmental contaminants. Environ. Sci. Technol. 45, 8506. doi:10.1021/es2019324.

De Corte, S., Sabbe, T., Hennebel, T., Vanhaecke, L., De Gusseme, B., Verstraete, W., Boon, N., 2012. Doping of biogenic Pd catalysts with au enables dechlorination of diclofenac at environmental conditions. Water Res. 46, 2718–2726. doi:10.1016/j.watres.2012.02.036.

de Pedro, Z.M., Diaz, E., Mohedano, A.F., Casas, J.A., Rodriguez, J.J., 2011. Compared activity and stability of Pd/Al_2O_3 and Pd/AC catalysts in 4-Chlorophenol hydrodechlorination in different pH media. Appl. Catal. B Environ. 103, 128–135. doi:10.1016/j.apcatb.2011.01.018.

de Wit, C.A., 2002. An overview of brominated flame retardants in the environment. Chemosphere 46, 583–624. doi:10.1016/S0045-6535(01)00225-9.

Diaz, E., Mohedano, A.F., Casas, J.A., Calvo, L., Gilarranz, M.A., Rodriguez, J.J., 2015. Deactivation of a Pd/AC catalyst in the hydrodechlorination of chlorinated herbicides. Catal. Today 241, 86–91. doi:10.1016/j.cattod.2014.03.052.

Díaz, E., Casas, J.A., Mohedano, Á.F., Calvo, L., Gilarranz, M.A., Rodríguez, J.J., 2008. Kinetics of the hydrodechlorination of 4-chlorophenol in water using Pd, Pt, and Rh/Al_2O_3 catalysts. Ind. Eng. Chem. Res. 47, 3840–3846. doi:10.1021/ie071517n.

Díaz, E., Casas, J.A., Mohedano, Á.F., Calvo, L., Gilarranz, M.A., Rodríguez, J.J., 2009. Kinetics of 4-chlorophenol hydrodechlorination with alumina and activated carbon-supported Pd and Rh catalysts. Ind. Eng. Chem. Res. 48, 3351–3358. doi:10.1021/ie801462b.

Diaz, E., Cebrian, M., Bahamonde, A., Faraldos, M., Mohedano, A.F., Casas, J.A., Rodriguez, J.J., 2016. Degradation of organochlorinated pollutants in water by catalytic hydrodechlorination and photocatalysis. Catal. Today 266, 168–174. doi:10.1016/j.cattod.2015.08.013.

Diaz, E., Mohedano, A.F., Casas, J.A., Rodriguez, J.J., 2016. Analysis of the deactivation of pd, pt and rh on activated carbon catalysts in the hydrodechlorination of the MCPA herbicide. Appl. Catal. B Environ. 181, 429–435. doi:10.1016/j.apcatb.2015.08.008.

Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption 2020.

Dong, H., Xu, L., Mao, Y., Wang, Y., Duan, S., Lian, J., et al., 2021. Effective abatement of 29 pesticides in full-scale advanced treatment processes of drinking water: from concentration to human exposure risk. J. Hazard. Mater. 403, 123986. doi:10.1016/j.jhazmat.2020.123986.

Ebele, A.J., Abou-Elwafa Abdallah, M., Harrad, S., 2017. Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment. Emerg. Contam. 3, 1–16. doi:10.1016/j.emcon.2016.12.004.

Egorova, K.S., Ananikov, V.P., 2016. Which metals are green for catalysis? Comparison of the toxicities of Ni, Cu, Fe, Pd, Pt, Rh, and Au salts. Angew. Chem. Int. Ed. 55, 12150–12162. doi:10.1002/anie.201603777.

Elfikrie, N., Ho, Y.B., Zaidon, S.Z., Juahir, H., Tan, E.S.S., 2020. Occurrence of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers in Tengi River Basin. Malays. Sci. Total Environ. 712, 136540. doi:10.1016/j.scitotenv.2020.136540.

Evlampidou, I., Laia, Font-Ribera, David, Rojas-Rueda, Esther, Gracia-Lavedan, Nathalie, C., Neil, P., et al., 2020. Trihalomethanes in drinking water and bladder cancer burden in the European Union. Environ. Health Perspect. 128, 017001. doi:10.1289/EHP4495.

Freire, C., Soler, R., Fernandez, M.F., Villanueva, C.M., Grimalt, J.O., Olea, N., 2008. Valores de trihalometanos en agua de consumo de la provincia de Granada. España. Sanit. 22, 520–526.

Gavrilescu, M., Demnerová, K., Aamand, J., Agathos, S., Fava, F., 2015. Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. N. Biotechnol. 32, 147–156. doi:10.1016/j.nbt.2014.01.001.

Gilca, A.F., Teodosiu, C., Fiore, S., Musteret, C.P., 2020. Emerging disinfection byproducts: a review on their occurrence and control in drinking water treatment processes. Chemosphere 259, 127476. doi:10.1016/j.chemosphere.2020.127476.

Golubina, E.V., Lokteva, E.S., Lunin, V.V., Telegina, N.S., Stakheev, A.Y., Tundo, P., 2006. The role of Fe addition on the activity of Pd-containing catalysts in multiphase hydrodechlorination. Appl. Catal. A: Gen. 302, 32–41. doi:10.1016/j.apcata.2005.12.020.

Gómez-Sainero, L.M., Seoane, X.L., Fierro, J.L.G., Arcoya, A., 2002. Liquid-phase hydrodechlorination of CCl4 to CHCl3 on pd/carbon catalysts: nature and role of Pd active species. J. Catal. 209, 279–288. doi:10.1006/jcat.2002.3655.

Guzzella, L., Feretti, D., Monarca, S., 2002. Advanced oxidation and adsorption technologies for organic micropollutant removal from lake water used as drinking-water supply. Water Res. 36, 4307–4318. doi:10.1016/S0043-1354(02)00145-8.

Han, B., Liu, W., Li, J., Wang, J., Zhao, D., Xu, R., Lin, Z., 2017. Catalytic hydrodechlorination of triclosan using a new class of anion-exchange-resin supported Palladium catalysts. Water Res. 120, 199–210. doi:10.1016/j.watres.2017.04.059.

Heck, K.N., Nutt, M.O., Alvarez, P., Wong, M.S., 2009. Deactivation resistance of Pd/Au nanoparticle catalysts for water-phase hydrodechlorination. J. Catal. 267, 97–104. doi:10.1016/j.jcat.2009.07.015.

Herrero-Hernández, E., Andrades, M.S., Álvarez-Martín, A., Pose-Juan, E., Rodríguez-Cruz, M.S., Sánchez-Martín, M.J., 2013. Occurrence of pesticides and some of their degradation products in waters in a Spanish wine region. J. Hydrol. 486, 234–245. doi:10.1016/j.jhydrol.2013.01.025.

Hua, G., Reckhow, D.A., 2007. Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size. Environ. Sci. Technol. 41, 3309–3315. doi:10.1021/es062178c.

Huerta-Fontela, M., Galceran, M.T., Ventura, F., 2011. Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. Water Res. 45, 1432–1442. doi:10.1016/j.watres.2010.10.036.

Hung, Y., Waters, B.W., Yemmireddy, V.K., Huang, C., 2017. pH effect on the formation of THM and HAA disinfection byproducts and potential control strategies for food processing. J. Integr. Agric. 16, 2914–2923. doi:10.1016/S2095-3119(17)61798-2.

Rook, J.J., 1974. Formation of haloforms during chlorination of natural waters. J. Water Treat. Exam. 23, 234–243.

Jones, O.A., Lester, J.N., Voulvoulis, N., 2005. Pharmaceuticals: a threat to drinking water? Trends in Biotechnol. 23, 163–167. doi:10.1016/j.tibtech.2005.02.001.

Jurado, A., Walther, M., Díaz-Cruz, M.S., 2019. Occurrence, fate and environmental risk assessment of the organic microcontaminants included in the watch lists set by EU Decisions 2015/495 and 2018/840 in the groundwater of Spain. Sci. Tot. Environ. 663, 285–296. doi:10.1016/j.scitotenv.2019.01.270.

Keane, M.A., 2011. Supported transition metal catalysts for hydrodechlorination reactions. ChemCatChem 3, 800–821. doi:10.1002/cctc.201000432.

Klarich, K.L., Pflug, N.C., DeWald, E.M., Hladik, M.L., Kolpin, D.W., Cwiertny, D.M., LeFevre, G.H., 2017. Occurrence of neonicotinoid insecticides in finished drinking water and fate during drinking water treatment. Environ. Sci. Technol. Lett. 4, 168–173. doi:10.1021/acs.estlett.7b00081.

Koekemoer, A., Luckos, A., 2015. Effect of material type and particle size distribution on pressure drop in packed beds of large particles: extending the Ergun equation. Fuel 158, 232–238. doi:10.1016/j.fuel.2015.05.036.

Kopinke, F., Mackenzie, K., Koehler, R., Georgi, A., 2004. Alternative sources of hydrogen for hydrodechlorination of chlorinated organic compounds in water on pd catalysts. Appl. Catal. A Gen. 271, 119–128. doi:10.1016/j.apcata.2004.02.052.

Kurajica, L., Bošnjak, Ujević, M, Novak Stankov, M, Kinsela, A, S., Štiglić, J., Waite, D.T., Capak, K., 2020. Disinfection by-products in croatian drinking water supplies with special emphasis on the water supply network in the city of zagreb. J. Environ. Manag. 276, 111360. doi:10.1016/j.jenvman.2020.111360.

Lan, L., Liu, Y., Liu, S., Ma, X., Li, X., Dong, Z., Xia, C., 2019. Effect of the supports on catalytic activity of pd catalysts for liquid-phase hydrodechlorination/hydrogenation reaction. Environ. Technol. 40 (12), 1615–1623. doi:10.1080/09593330.2018.1426645.

Leone, V.O., Pereira, M.C., Aquino, S.F., Oliveira, L.C.A., Correa, S., Ramalho, T.C., et al., 2018. Adsorption of diclofenac on a magnetic adsorbent based on maghemite: experimental and theoretical studies. N. J. Chem. 42, 437–449. doi:10.1039/c7nj03214e.

Li, X., Ying, G., Su, H., Yang, X., Wang, L., 2010. Simultaneous determination and assessment of 4-nonylphenol, bisphenol A and triclosan in tap water, bottled water and baby bottles. Environ. Int. 36, 557–562. doi:10.1016/j.envint.2010.04.009.

Liu, M., Yin, H., Wu, Q., 2019. Occurrence and health risk assessment of pharmaceutical and personal care products (PPCPs) in tap water of shanghai. Ecotoxicol. Ecotoxicol. Environ. Saf. 183, 109497. doi:10.1016/j.ecoenv.2019.109497.

Liu, X., Zhong, J., Fang, L., Wang, L., Ye, M., Shao, Y., et al., 2016. Trichloroacetic acid reduction by an advanced reduction process based on carboxyl anion radical. Chem. Eng. J. 303, 56–63. doi:10.1016/j.cej.2016.05.130.

Lonappan, L., Brar, S.K., Das, R.K., Verma, M., Surampalli, R.Y., 2016. Diclofenac and its transformation products: environmental occurrence and toxicity - A review. Environ. Int. 96, 127–138. doi:10.1016/j.envint.2016.09.014.

Lowry, G., Reinhard, M., 2000. Pd-catalyzed TCE dechlorination in groundwater: solute effects, biological control, and oxidative catalyst regeneration. Environ. Sci. Technol. 34, 3217–3223. doi:10.1021/es991416j.

Luo, Y., Zhou, C., Bi, Y., Long, X., Wang, B., Tang, Y., et al., 2020. Long-term continuous co-reduction of 1,1,1-trichloroethane and trichloroethene over palladium nanoparticles spontaneously deposited on H2-transfer membranes. Environ. Sci. Technol. 55, 2057–2066. doi:10.1021/acs.est.0c05217.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, Long Duc, Hai, F.I., Zhang, J., et al., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci. Tot. Environ. 473, 619–641. doi:10.1016/j.scitotenv.2013.12.065.

Mackenzie, K., Frenzel, H., Kopinke, F., 2006. Hydrodehalogenation of halogenated hydrocarbons in water with pd catalysts: reaction rates and surface competition. Appl. Catal. B: Environ. 63 (3), 161–167. doi:10.1016/j.apcatb.2005.10.004.

McHugh, B., Poole, R., Corcoran, J., Anninou, P., Boyle, B., Joyce, E., et al., 2010. The occurrence of persistent chlorinated and brominated organic contaminants in the european eel (anguilla anguilla) in Irish waters. Chemosphere 79, 305–313. doi:10.1016/j.chemosphere.2010.01.029.

Mendes, L.D., Bernardi, G., Elias, W.C., de Oliveira, D.C., Domingos, J.B., Carasek, E., 2021. A green approach to DDT degradation and metabolite monitoring in water comparing the hydrodechlorination efficiency of Pd, Au-on-Pd and Cu-on-Pd nanoparticle catalysis. Sci. Tot. Environ. 760, 143403. doi:10.1016/j.scitotenv.2020.143403.

Miyabe, K., Taniguchi, N., Imura, A., Tezuka, Y., 2003. Kinetic study of the hydrodechlorination of trichloroethene in water using a Platinum catalyst and hydrazine. Water Environ. Res. 75, 472–477. doi:10.2175/106143003X141277.

Molina, C.B., Pizarro, A.H., Casas, J.A., Rodriguez, J.J., 2014. Aqueous-phase hydrodechlorination of chlorophenols with pillared clays-supported Pt, Pd and Rh catalysts. Appl. Catal. B: Environ. 148, 330–338. doi:10.1016/j.apcatb.2013.11.010.

Moradi, S., Liu, S., Chow, C.W.K., van Leeuwen, J., Cook, D., Drikas, M., Amal, R., 2017. Chloramine demand estimation using surrogate chemical and microbiological parameters. J. Environ. Sci. 57, 1–7. doi:10.1016/j.jes.2017.01.010.

Müller, A., Ludwig, M., Arlit, M., Lange, R., 2015. Evaluation of reactor concepts for the continuous production of fine chemicals using the selective hydrogenation of cinnamaldehyde over Palladium catalysts. Catal. Today 241, 214–220. doi:10.1016/j.cattod.2013.12.051.

Munoz, M., de Pedro, Z.M., Casas, J.A., Rodriguez, J.J., 2011. Assessment of the generation of chlorinated byproducts upon Fenton-like oxidation of chlorophenols at different conditions. J. Hazard. Mat. 190, 993–1000. doi:10.1016/j.jhazmat.2011.04.038.

Munoz, M., de Pedro, Z.M., Casas, J.A., Rodriguez, J.J., 2014. Improved gamma-alumina-supported Pd and Rh catalysts for hydrodechlorination of chlorophenols. Appl. Catal. A Gen. 488, 78–85. doi:10.1016/j.apcata.2014.09.035.

Munoz, M., Ponce, S., Zhang, G., Etzold, B.J.M., 2016. Size-controlled PtNi nanoparticles as highly efficient catalyst for hydrodechlorination reactions. Appl. Catal. B: Environ. 192, 1–7. doi:10.1016/j.apcatb.2016.03.038.

Nangoi, I.M., Kiyohara, P.K., Rossi, L.M., 2010. Catalytic hydrodechlorination of chlorobenzene over supported Palladium catalyst in buffered medium. Appl. Catal. B: Environ. (1) 42–46. doi:10.1016/j.apcatb.2010.07.008.

Nieto-Sandoval, J., Munoz, M., de Pedro, Z.M., Casas, J.A., 2018. Fast degradation of diclofenac by catalytic hydrodechlorination. Chemosphere 213, 141–148. doi:10.1016/j.chemosphere.2018.09.024.

Nieto-Sandoval, J., Ortiz, D., Munoz, M., de Pedro, Z.M., Casas, J.A., 2019a. On the deactivation and regeneration of Pd/Al$_2$O$_3$ catalyst for aqueous-phase hydrodechlorination of diluted chlorpromazine solution. Catal. Today 356, 255–259. doi:10.1016/j.cattod.2019.06.028.

Nieto-Sandoval, J., Munoz, M., de Pedro, Z.M., Casas, J.A., 2019b. Catalytic hydrodechlorination as polishing step in drinking water treatment for the removal of chlorinated micropollutants. Sep. Purif. Technol. 227, 115717. doi:10.1016/j.seppur.2019.115717.

Nieto-Sandoval, J., Gomez-Herrero, E., Morabet, El, F, Munoz, M, de Pedro, Z, M., Casas, J.A., 2020a. Catalytic hydrodehalogenation of haloacetic acids: a kinetic study. Ind. Eng. Chem. Res. 59, 17779–17785. doi:10.1021/acs.iecr.0c03495.

Nieto-Sandoval, J., Rodriguez, M., Munoz, M., de Pedro, Z.M., Casas, J.A., 2020b. Catalyst deactivation in the hydrodechlorination of micropollutants. A case of study with neonicotinoid pesticides. J. Water Process. Eng. 38, 101550. doi:10.1016/j.jwpe.2020.101550.

Nieto-Sandoval, J., Sanchez, R., Munoz, M., de Pedro, Z.M., Casas, J.A., 2021a. Catalytic hydrodehalogenation of the flame retardant tetrabromobisphenol A by alumina-supported Pd, Rh and Pt catalysts. Chem. Eng. J. Adv. 9, 100212. doi:10.1016/j.ceja.2021.100212.

Nieto-Sandoval, J., Gomez-Herrero, E., Munoz, M., de Pedro, Z.M., Casas, J.A., 2021b. Palladium-based catalytic membrane reactor for the continuous flow hydrodechlorination of chlorinated micropollutants. Appl. Catal. B: Environ. 293, 120235. doi:10.1016/j.apcatb.2021.120235.

Niu, Z., Hu, X., Zhang, Y., Sun, Y., 2016. Effect of chlorine dosage in prechlorination on trihalomethanes and haloacetic acids during water treatment process. Environ. Sci. Pollut. Res. 24, 5068–5077. doi:10.1007/s11356-016-8265-x.

Ordóñez, S., Díaz, E., Diez, F.V., Sastre, H., 2007. Regeneration of Pd/Al$_2$O$_3$ catalysts used for tetrachloroethylene hydrodechlorination. React. Kinet. Catal. Lett. 90, 101–106. doi:10.1007/s11144-007-5024-5.

Ozturk, E., 2018. Applying analytical decision methods for determination of the best treatment alternative to remove emerging micropollutants from drinking water and wastewater: triclosan example. Environ. Sci. Pollut. Res. 25, 30517–30546. doi:10.1007/s11356-018-3036-5.

Padhye, L.P., Yao, H., Kung'u, F.T., Huang, C., 2014. Year-long evaluation on the occurrence and fate of pharmaceuticals, personal care products, and endocrine disrupting chemicals in an urban drinking water treatment plant. Water Res. 51, 266–276. doi:10.1016/j.watres.2013.10.070.

Perez-Estrada, L.A., Malato, S., Gernjak, W., Aguera, A., Thurman, E.M., Ferrer, I., Fernandez-Alba, A.R., 2005. Photo-fenton degradation of diclofenac: identification of main intermediates and degradation pathway. Environ. Sci. Technol. 39, 8300–8306. doi:10.1021/es050794n.

Pérez-Moya, M., Graells, M., Valle, del, L, J., Centelles, E., Mansilla, H.D., 2007. Fenton and Photo-fenton degradation of 2-Chlorophenol: multivariate analysis and toxicity monitoring. Catal. Today 124, 163–171. doi:10.1016/j.cattod.2007.03.034.

Poerschmann, J., Trommler, U., Gorecki, T., Kopinke, F., 2009. Formation of chlorinated biphenyls, diphenyl ethers and benzofurans as a result of Fenton-driven oxidation of 2-chlorophenol. Chemosphere 75 (6), 772–780. doi:10.1016/j.chemosphere.2009.01.020.

Postigo, C., Emiliano, P., Barceló, D., Valero, F., 2018. Chemical characterization and relative toxicity assessment of disinfection byproduct mixtures in a large drinking water supply network. J. Hazard. Mater. 359, 166–173. doi:10.1016/j.jhazmat.2018.07.022.

Reis, E.O., Foureaux, A.F.S., Rodrigues, J.S., Moreira, V.R., Lebron, Y.A.R., Santos, L.V.S., et al., 2019. Occurrence, removal and seasonal variation of pharmaceuticals in brasilian drinking water treatment plants. Environ. Pollut. 250, 773–781. doi:10.1016/j.envpol.2019.04.102.

Rizzo, L., Belgiorno, V., Gallo, M., Meriç, S., 2005. Removal of THM precursors from a high-alkaline surface water by enhanced coagulation and behaviour of THMFP toxicity on D. magna. Desalination 176, 177–188. doi:10.1016/j.desal.2004.10.020.

Rubirola, A., Santos, F.J., Boleda, M.R., Galceran, M.T., 2018. Routine method for the analysis of short-chain chlorinated paraffins in surface water and wastewater. CLEAN–Soil Air Water 46, 1600151. doi:10.1002/clen.201600151.

Schmidt, C.K., Brauch, H.J., 2008. N,N-dimethylsulfamide as precursor for N-nitrosodimethylamine (NDMA) formation upon ozonation and its fate during drinking water treatment. Environ. Sci. Technol. 42, 6340–6346. doi:10.1021/es7030467.

Shemer, H., Narkis, N., 2005. Trihalomethanes aqueous solutions sono-oxidation. Water Res. 39 (12), 2704–2710. doi:10.1016/j.watres.2005.04.043.

Singer, H., Müller, S., Tixier, C., Pillonel, L., 2002. Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: Field measurements in wastewater treatment plants, surface waters, and lake sediments. Environ. Sci. Technol. 36, 4998–5004. doi:10.1021/es025750i.

Sjerps, R.M.A., Kooij, P.J.F., van Loon, A., Van Wezel, A.P., 2019. Occurrence of pesticides in dutch drinking water sources. Chemosphere 235, 510–518. doi:10.1016/j.chemosphere.2019.06.207.

Srivastav, A.L., Patel, N., Chaudhary, V.K., 2020. Disinfection by-products in drinking water: occurrence, toxicity and abatement. Environ. Pollut. 267, 115474. doi:10.1016/j.envpol.2020.115474.

Stackelberg, P.E., Gibs, J., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Lippincott, R.L., 2007. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Sci. Tot. Environ. 377, 255–272. doi:10.1016/j.scitotenv.2007.01.095.

Sun, M., Zhou, H., Xu, B., Bao, J., 2018. Distribution of perfluorinated compounds in drinking water treatment plant and reductive degradation by UV/SO32− process. Environ. Sci. Pollut. Res. 25, 7443–7453. doi:10.1007/s11356-017-1024-9.

Sun, Y., Wu, Q., Hu, H., Tian, J., 2009. Effect of bromide on the formation of disinfection by-products during wastewater chlorination. Water Res. 43, 2391–2398. doi:10.1016/j.watres.2009.02.033.

Tomizawa, M., Casida, J., 2005. Neonicotinoid insecticide toxicology: mechanisms of selective action. Annu. Rev. Pharmacol. Toxicol. 45, 247–268. doi:10.1146/annurev.pharmtox.45.120403.095930.

US Environmental Protection Agency, 2006. National primary drinking water regulations: stage 2 disinfectants and disinfection byproducts rule. Fed. Regist. 71, 387–493.

Vieno, N.M., Härkki, H., Tuhkanen, T., Kronberg, L., 2007. Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. Environ, Sci. Technol. 41, 5077–5084. doi:10.1021/es062720x.

Wan, Y., Wang, Y., Xia, W., He, Z., Xu, S., 2019. Neonicotinoids in raw, finished, and tap water from Wuhan, central China: assessment of human exposure potential. Sci. Tot. Environ. 675, 513–519. doi:10.1016/j.scitotenv.2019.04.267.

Wang, S., Yang, B., Zhang, T., Yu, G., Deng, S., Huang, J., 2010. Catalytic hydrodechlorination of 4-chlorophenol in an aqueous solution with Pd/Ni catalyst and formic acid. Eng. Chem. Res. 49, 4561–4565. doi:10.1021/ie9005194.

Wang, X., Li, J., Fu, M., Yuan, B., Cui, H., Wang, Y., 2015a. Fabrication and evaluation of Au–Pd core-shell nanocomposites for dechlorination of diclofenac in water. Environ. Technol. 36, 1510–1518. doi:10.1080/09593330.2014.994044.

Wang, X., Wang, Y., Yuan, B., Cui, H., Fu, M., 2015b. Fabrication of resin supported Au–Pd bimetallic nanoparticle composite to efficiently remove chloramphenicol from water. RSC Adv. 5, 18806–18812. doi:10.1039/C4RA17309K.

Whitehorn, P., O'Connor, S., Wäckers, F., Goulson, D., 2012. Neonicotinoid pesticide reduces bumble bee colony growth and queen production. Science 336, 351–352. doi:10.1126/science.1215025.

Williams, C.J., Conrad, D., Kothawala, D.N., Baulch, H.M., 2019. Selective removal of dissolved organic matter affects the production and speciation of disinfection byproducts. Sci. Tot. Environ. 652, 75–84. doi:10.1016/j.scitotenv.2018.10.184.

Wing, L.H., Ling, J., Si, W., Tsui Mirabelle, M.P., Bingsheng, Z., Liping, J., et al., 2013. Pharmaceuticals in tap water: human health risk assessment and proposed monitoring framework in china. Environ. Health Perspect. 121, 839–846. doi:10.1289/ehp.1206244.

Wu, K., Qian, X., Chen, L., Xu, Z., Zheng, S., Zhu, D., 2015. Effective liquid phase hydrodechlorination of diclofenac catalysed by Pd/CeO_2. Rsc Adv. 5, 18702–18709. doi:10.1039/c4ra16674d.

Wu, W., Xu, J., Ohnishi, R., 2005. Complete hydrodechlorination of chlorobenzene and its derivatives over supported nickel catalysts under liquid phase conditions. Appl. Catal. B Environ. 60, 129–137. doi:10.1016/j.apcatb.2005.03.003.

Xia, C., Liu, Y., Zhou, S., Yang, C., Liu, S., Xu, J., et al., 2009. The Pd-catalyzed hydrodechlorination of chlorophenols in aqueous solutions under mild conditions: a promising approach to practical use in wastewater. J. Hazard. Mat. 169, 1029–1033. doi:10.1016/j.jhazmat.2009.04.043.

Xiong, J., Ma, Y., Yang, W., Zhong, L., 2018. Rapid, highly efficient and stable catalytic hydrodechlorination of chlorophenols over novel Pd/CNTs-Ni foam composite catalyst in continuous-flow. J. Hazard. Mat. 355, 89–95. doi:10.1016/j.jhazmat.2018.05.018.

Yang, M., Zhang, X., 2013. Comparative developmental toxicity of new aromatic halogenated DBPs in a chlorinated saline sewage effluent to the marine Polychaete Platynereis dumerilii. Environ. Sci. Technol. 47, 10868–10876. doi:10.1021/es401841t.

Yu, X., Wu, T., Yang, X., Xu, J., Auzam, J., Semiat, R., Han, Y., 2016. Degradation of trichloroethylene by hydrodechlorination using formic acid as hydrogen source over supported pd catalysts. J. Hazard. Mat. 305, 178–189. doi:10.1016/j.jhazmat.2015.11.025.

Yuan, G., Keane, M.A., 2004. Role of base addition in the liquid-phase hydrodechlorination of 2,4-dichlorophenol over Pd/Al_2O_3 and Pd/C. J. Catal. 225, 510–522. doi:10.1016/j.jcat.2004.05.003.

Yuan, G., Keane, M.A., 2003. Catalyst deactivation during the liquid phase hydrodechlorination of 2,4-dichlorophenol over supported Pd: influence of the support. Catal. Today 88, 27–36. doi:10.1016/j.cattod.2003.08.004.

Zhao, J., Ying, G., Liu, Y., Chen, F., Yang, J., Wang, L., 2010. Occurrence and risks of triclosan and triclocarban in the Pearl river system, south China: from source to the receiving environment. J. Hazard. Mat. 179, 215–222. doi:10.1016/j.jhazmat.2010.02.082.

Zhao, X., Hou, Y., Liu, H., Qiang, Z., Qu, J., 2009. Electro-oxidation of diclofenac at boron doped diamond: kinetics and mechanism. Electrochim. Acta 54, 4172–4179. doi:10.1016/j.electacta.2009.02.059.

Zheng, C., Li, M., Liu, H., Xu, Z., 2020. Complete dehalogenation of bromochloroacetic acid by liquid phase catalytic hydrogenation over Pd/CeO_2 catalysts. Chemosphere 239, 124740. doi:10.1016/j.chemosphere.2019.124740.

Zhou, J., Han, Y., Wang, W., Xu, Z., Wan, H., Yin, D., et al., 2013. Reductive removal of chloroacetic acids by catalytic hydrodechlorination over Pd/ZrO_2 catalysts. Appl. Catal. B Environ. 134-135, 222–230. doi:10.1016/j.apcatb.2013.01.005.

Zhou, T., Li, Y., Lim, T., 2010. Catalytic hydrodechlorination of chlorophenols by Pd/Fe nanoparticles: comparisons with other bimetallic systems, kinetics and mechanism. Sep. Purif. Technol. 76, 206–214. doi:10.1016/j.seppur.2010.10.010.