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Catalytic hydrodehalogenation of the flame retardant tetrabromobisphenol A by alumina-supported Pd, Rh and Pt catalysts

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ABSTRACT

Tetrabromobisphenol A (TBBPA) is one of the most used BFRs, being characterized by a strong persistence and leading to negative effects on both the environment and human health. The aim of this work is to evaluate the feasibility of aqueous-phase catalytic hydrodehalogenation (HDH) for the fast and environmentally-friendly degradation of the brominated flame retardant TBBPA. Pd, Rh, and Pt on alumina commercial catalysts (1% wt.) were tested and reactions were performed under ambient operating conditions. TBBPA (1 mg L^{-1}) was completely removed in short reaction times (< 5 min) using the Pd catalyst while longer reaction times were required in the case of Rh and Pt catalysts as active phase. Furthermore, although TBBPA suffered a strong adsorption on the catalyst surface, both adsorbed and free molecules reacted. Bromine balance was closed (> 95%) in 15 min using Pd/Al_2O_3. Nevertheless, employing Rh and Pt alumina-supported catalysts debromination of TBBPA increased progressively requiring much longer times and only 83% and 78% debromination yields were achieved after 2 h reaction, respectively. Bisphenol A (BPA), a well-known endocrine disruptor, was generated as reaction intermediate but it was further hydrogenated with both Pd and Rh catalysts, whereas it remained as reaction product with the Pt catalyst. A series reaction pathway considering both hydro-debromination and hydrogenation steps was proposed based on the obtained results. The experimental data obtained with the Pd/Al_2O_3 catalyst were successfully described by a pseudo-first order kinetic model, obtaining an apparent activation energy of 36 kJ mol^{-1}. Notably, this catalyst showed a reasonable stability after three consecutive HDH runs.

1. Introduction

Brominated flame retardants (BFRs) are compounds widely used in industry for materials protection against ignition. Accordingly, BFRs are usually incorporated as additives in plastics, textiles and electronic devices [1]. However, these useful chemicals for the industry and general society are associated to significant negative effects on the environment [2,3]. Among BFRs, tetrabromobisphenol A (TBBPA), synthesized by bromination of bisphenol A (BPA), is one of the most current-use BFRs [4]. Due to its widespread use and high persistence, TBBPA has been frequently detected in the environment such as soil, dust, air and water [5]. In general, TBBPA is discharged into the aquatic environment from the migration of products and from wastewater treatment plants which are not able to remove completely this kind of pollutant. Moreover, TBBPA has been detected in surface water which is then used as raw source in drinking water treatment plants (DWTPs). For instance, TBBPA has been identified in river and lakes in China at a concentration in the range from < 10 ng L^{-1} to 4800 ng L^{-1} [6]. The presence of this pollutant represents a threat to the public health. In this sense, TBBPA has been detected in humans such as in breast milk and can induce immunotoxicity, neurotoxicity, disruption of endocrine function and cytotoxicity [7,8].

Conventional DWTPs are not specifically designed for the removal of organohalogenated micropollutants. Sacher et al. evaluated the fate of ten brominated and chlorinated flame retardants along different steps of the typical drinking water treatment [9]. The authors demonstrated that conventional processes are not an efficient option for their complete elimination and identified adsorption onto activated carbon as a promising solution. Nevertheless, this process requires further management of the saturated adsorbent and thus, other technologies have been investigated in the literature for TBBPA removal. Advanced oxidation processes, photochemical degradation and biological methods have received major attention but they show some disadvantages such as to the high cost of the reagents/energy input, the formation of even

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more harmful intermediates and/or the relatively low efficiency [10–14].

Aqueous-phase catalytic hydrodehalogenation (HDH) is emerging as a potential technology for the removal of a wide range of organohalogenated micropollutants [15,16]. This system consists in the reaction of the pollutant with hydrogen in the presence of a catalyst, leading to the generation of halogen-free compounds and the corresponding hydrohalic acids. Precious metals such as Pd, Pt or Rh are the most common active phases used in HDH reactions [17,18]. Pt catalysts have showed high activity in HDH reactions, but a progressive deactivation was observed during the HDH of chlorophenols due to the adsorption of chlorinated species over the active sites of the catalyst [17]. Rh-based catalysts are active and stable for hydrodehalogenation and hydrogenation steps, allowing to form also hydrogenated compounds [18]. Pd catalysts are the most used in HDH reactions due to its high activity and resistance to HCl poisoning [19,20]. Regarding the support, some materials such as activated carbon or alumina have shown adequate properties due to their high surface area [21]. Recent works have demonstrated the high efficiency of this environmentally-friendly process for the removal of organohalogenated pharmaceuticals, pesticides, personal care products and disinfection-byproducts, among others, showing that this transformation allows to reduce significantly the ecotoxicity of the effluent [22]. To the best of our knowledge, few works have dealt with the removal of brominated flame retardants by HDH technology [23,24]. Among them, Wu et al. evaluated Pd catalysts over different supports (TiO_2, CeO_2, Al_2O_3 and SiO_2) for the removal of TBBPA by HDH, which followed a stepwise debromination reaction [25]. Nevertheless, the effect of the active phases on the activity and selectivity of the process for TBBPA removal has not been investigated so far.

This work aims to evaluate the feasibility of HDH for the removal of TBBPA using three different alumina-supported catalysts with Pd, Rh and Pt as active phases given their prominent role in this field [18]. A complete operating conditions study was carried out to evaluate the effect of catalyst load, rection temperature and H_2 flow. Based on the species identified, a reaction pathway was accordingly proposed and a kinetic model was also developed. The stability of the most promising catalyst was finally evaluated upon consecutive HDH runs.

2. Materials and methods

2.1. Materials

Tetrabromobisphenol A (≥ 99%) and bisphenol A (≥ 98%) were supplied by Sigma-Aldrich. The chemical structures of the micropollutants tested in this work are collected in Table 1. Acetonitrile (99.9%), sodium hypobromite (10% w/v) and methanol (supragradient HPLC grade) were provided by Scharlau. Acetic acid (99.5%) was and Hydrogen (99.999%) was delivered by Panreac and Praxair, respectively. The commercial catalysts Pd/Al_2O_3 (Lot: U20A021), Rh/Al_2O_3 (Lot: U27A030) and Pt/Al_2O_3 (Lot: M15F051) (1% wt.) were supplied by Alfa Aesar in powder form (mean particle size of the catalysts was in the range from 45.3 to 47.5 μm). All the experiments were carried out using deionized water.

2.2. Experimental procedure

Experiments were operated batch-wise in a magnetically stirred glass slurry-type reactor (500 mL) under continuous feeding with H_2 at 50 N mL min^{-1} in a reaction volume of 450 mL. Due to the low solubility of TBBPA in water [7], a previous concentrated solution of TBBPA in methanol was prepared and diluted in water for subsequent experiments. Initial concentration of TBBPA for HDH reactions was fixed at 1000 μg L^{-1}. Although it is somehow higher than the real water concentrations [6], it allowed to warrant an accurate quantification of the target pollutant and intermediates. The catalyst concentration was evaluated in the range from 0.25 to 1 g L^{-1}. HDH runs were carried out at different temperatures from 15 to 35 °C. In addition, the impact of the H_2 flow was evaluated in the range from 10 to 50 N mL min^{-1}. According to our previous work, the stirring velocity was fixed at 900 rpm in order to avoid external mass transfer limitations [26].

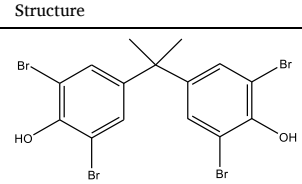
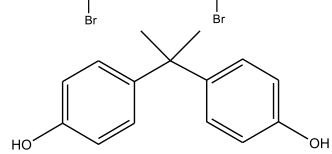
2.3. Analytical methods

The evolution of the HDH reactions was followed by withdrawing periodically liquid samples from the reactor, which were centrifuged prior analysis for catalyst separation. TBBPA and the resulting intermediates and products were quantified by HPLC-UV (Shimadzu, LC-2030C LT, Prominence-i model) using an Agilent Eclipse Plus C18 column (15 cm length, 0.46 cm diameter) as stationary phase. Analyses were performed at 270 nm using a mixture of methanol and water as mobile phase at 80/20 vol ratio. LC/MS analysis was used to identify the reaction intermediates and products by a SQ Agilent 6120 chromatograph equipped with a quadrupole detector using the same column and analysis conditions previously described. For data acquisition and processing, the software package LC/MSD ChemStation was used. HBr produced during reaction was quantified as bromide by a Metrohm 883 Basic IC Plus ion chromatograph. A Metrosep A supp 5–250 column (25 cm length, 0.4 cm internal diameter) was used as stationary phase and a 3.2 mM Na_2CO_3 aqueous solution as mobile phase.

2.4. Catalyst characterization

Catalysts were characterized by different techniques. The metal content was measured by inductively coupled plasma mass spectrometry (ICP-MS) using a NexION 300 X Perkin Elmer instrument. In order to determine the surface metal species (Me^0 and Me^{n+}) in the catalyst, X-ray photoelectron spectroscopy (XPS) was employed using a spectrometer PHI VersaProbe II equipped with a Al Kα X-ray excitation source, 1486.6 eV. The XPS-Peak software was used for peaks deconvolution and the area of the spectral peaks was used to calculate the surface metal species content. Fresh catalysts were characterized by transmission

Table 1
Chemical structure and molecular weight of the micropollutants tested in this work.

Compound	Abbreviation	Structure	Molecular weight (g mol^{-1})
Tetrabromobisphenol A	TBBPA		543.9
Bisphenol A	BPA		228.3

electron microscopy (TEM) using a JEOL JEM 3000 F microscopy with a point resolution of 0.17 nm. For measuring and counting the metal particles on TEM images, the software "ImageJ" was used (more than 100 particles were measured per sample). The surface area of the catalysts, previously outgassed overnight at 150 °C under vacuum conditions, was characterized by nitrogen adsorption–desorption at - 196 °C using a Micromeritics Tristar 3020 apparatus. The particle size was measured by an analyser Mastersizer 3000 Malvern Panalytical using the Fraunhofer dispersion model. The point of zero charge (pH_{PZC}) of the catalysts was determined following a method described elsewhere [27].

3. Results and discussion

3.1. Catalyst characterization

Table 2 collects the main properties of the three alumina-supported catalysts used in this work. ICP-MS analysis allowed to confirm that the metal content was close to 1% wt. in the three solids. From the XPS analyses (see Figs. S1–S3 of the Supplementary Material), the zerovalent (Me^0) and electrodeficient (Me^{n+}) ratios were calculated obtaining values of 1.04, 1.13 and 1.48 for Pd/Al_2O_3, Rh/Al_2O_3 and Pt/Al_2O_3, respectively. As reported Molina et al., the presence of both species improves the activity of the catalysts during HDH reactions [17]. The surface area of the catalysts was from 128 to 153 $m^2\ g^{-1}$ and the pH_{PZC} was close to 7.6 in all cases (see Fig. S4 of the Supplementary Material). Fig. 1 shows TEM images of the catalysts where the metal nanoparticles can be distinguished. Metal particle sizes within the 3, 4 nm range were obtained in the case of Pd and Pt catalysts, while Rh/Al_2O_3 catalyst was characterized by a lower metal particle size. All in all, metal particle sizes are close to the 2–4 nm optimum range for these precious metals in HDH reactions [28].

4.2. Catalytic hydrodebromination of TBBPA

Preliminary adsorption experiments using 1000 μg L^{-1} TBBPA and 1 g L^{-1} catalyst were carried out in the absence of H_2 (see Fig. S5 of the Supplementary Material). TBBPA adsorption yields onto the Pd/Al_2O_3, Rh/Al_2O_3 and Pt/Al_2O_3 catalysts were 70%, 79% and 81%, respectively. Considering these results, an initial adsorption stage of 15 min was included in the experimental procedure prior starting the reaction by the feeding of H_2 gas flow. Fig. 2 shows the evolution of HDH reactions with the three catalysts. As can be observed, TBBPA concentration sharply decreased along reaction, being completely removed in less than 30 min in all cases. However, bromide concentration just showed a sharp increase in the case of Pd/Al_2O_3, being the dibrorination stage considerably slower with Rh/Al_2O_3 and Pt/Al_2O_3 catalysts. A slight decrease in the pH value of the effluent from the initial (pH_0-6.9) to pH in the range from 6.5 to 6.7 was observed due to HBr release during the HDH of TBBPA. The prior adsorption of TBBPA onto the Pd/Al_2O_3 catalyst surface seems to favor high HDH rates. In fact, bromine balance was closed (> 95%) in less than 5 min with Pd/Al_2O_3 but it was not closed even at the end of the reaction (2 h) with Rh/Al_2O_3 and Pt/Al_2O_3 catalysts due to TBBPA was still adsorbed on the catalysts. Remarkably, no TBBPA brominated byproducts (B3BPA, B2BPA and BBPA) were identified, which are characterized by higher toxicity than the parent compound, being BPA the main intermediate formed by hydrodebromination [29]. In this sense, an additional experiment with BPA in absence of H_2 was performed using Pd/Al_2O_3 catalyst and no effect of BPA adsorption onto the catalyst was observed (See Fig. S6 of Supplementary Material). BPA, which is a well-known endocrine disruptor [30], was afterwards completely hydrogenated with Pd/Al_2O_3 and Rh/Al_2O_3 catalysts, while a progressive increase of its concentration was found with the Pt/Al_2O_3 catalyst. It must be noted that an additional partially hydrogenated compound was detected by HPLC-UV after BPA formation.

Table 2
Main properties of the Pd, Rh and Pt commercial catalysts.

Catalyst	Me (% wt.)	Me^0/Me^{n+}	Me particle size (nm)	Surface area ($m^2\ g^{-1}$)	pH_{PZC}
Pd/Al_2O_3	0.95	1.04	3.3	147	7.6
Rh/Al_2O_3	0.91	1.13	1.7	153	7.6
Pt/Al_2O_3	0.85	1.48	3.6	128	7.6

In order to identify the intermediates and products generated along the HDH reaction, a new set of experiments was carried out using a significantly higher initial concentration of TBBPA (10 mg L^{-1}). Different samples along the HDH reaction were analysed for the identification of their structures using LC/MS. Scheme 1 shows the reaction pathway proposed which was divided in two steps: hydrodebromination and hydrogenation. TBBPA was firstly hydrodebrominated to BPA. Afterwards, hydrogenation took place, being BPA transformed to a compound also identified by HPLC-UV where one aromatic ring has been partially hydrogenated. Subsequently, this partially hydrogenated ring was fully hydrogenated forming 2-(4-hydroxycyclohexyl)-2-(p-hydroxyphenyl)propane. Moreover, the product 4-ethylphenol was obtained via bond cleavage between the both rings, which is in agreement with previous works in the literature that reported the formation of phenolic compounds in the TBBPA debromination [31]. It must be noted that the other corresponding product from the bond cleavage (shown in Scheme 1) was not identified by LC/MS. These results are consistent with the reported by Yen et al. who investigated the hydrogenation of BPA using ruthenium-based catalysts [32].

4.3. Operating conditions study

A complete operating conditions study was carried out. Impact of H_2 flow in the reaction yield was evaluated at 10, 30 and 50 N mL min^{-1}, achieving in all cases similar TBBPA conversion and product distribution (data not shown). Thus, it can be assumed that H_2 was in high excess when the HDH reactions were carried out using H_2 flows above 10 N mL min^{-1} which allows to discard possible limitations related to the availability of hydrogen in the active centres of the catalyst.

Fig. 3 shows the evolution of TBBPA at different catalyst concentrations (0.25–1 g L^{-1}). Higher catalyst loads led to a proportional increase in the HDH rates. In the same line, BPA hydrogenation rate increased with increasing the catalyst load. Experimental data were accurately fitted by an apparent first order kinetic equation. Kinetic rate constant values of 0.19, 0.44 and 1.03 min^{-1} were obtained for the HDH of TBBPA using 0.25, 0.50 and 1 g L^{-1} catalyst concentrations, respectively. Therefore, TBBPA degradation rate linearly correlated with the catalyst load, which allowed to discard external mass transfer limitations under the operating conditions tested in this work (see Fig. S7 of Supplementary Material).

The effect of temperature was evaluated in the range of 15 to 35 °C. As expected, the temperature increase led to higher degradation rates. The values of the pseudo-first order kinetic constants obtained at 15, 25 and 35 °C were 0.85, 1.03 and 2.24 min^{-1}, respectively. The apparent activation energy for the HDH of TBBPA was calculated from the Arrhenius equation (see Fig. S8 of Supplementary Material), obtaining a value of 36 kJ mol^{-1}. This value is similar to those previously reported in the literature for the HDH of different organohalogenated compounds using Pd/Al_2O_3 catalysts [22]. These results allow to confirm that the HDH process is fast and effective for both hydrodechlorination and hydrodebromination reactions [33]. Nevertheless, hydrodebromination has been scarcely investigated for the treatment of organobromine micropollutants in water such as brominated flame retardants, pesticides and disinfection-byproducts. This work demonstrates the potential of hydrodebromination in water purification processes. Moreover, in the preoxidation step in conventional DWTPs, bromination reactions usually take place in waters with high bromide content and other organic

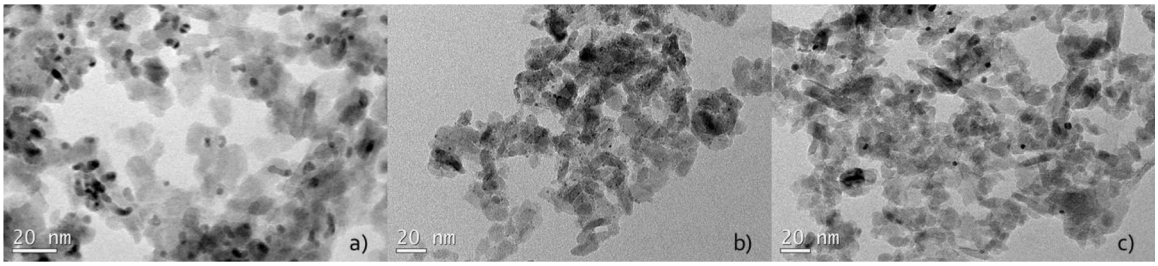


Fig. 1. TEM images of the catalysts (a) Pd/Al_2O_3, (b) Rh/Al_2O_3 and (c) Pt/Al_2O_3.

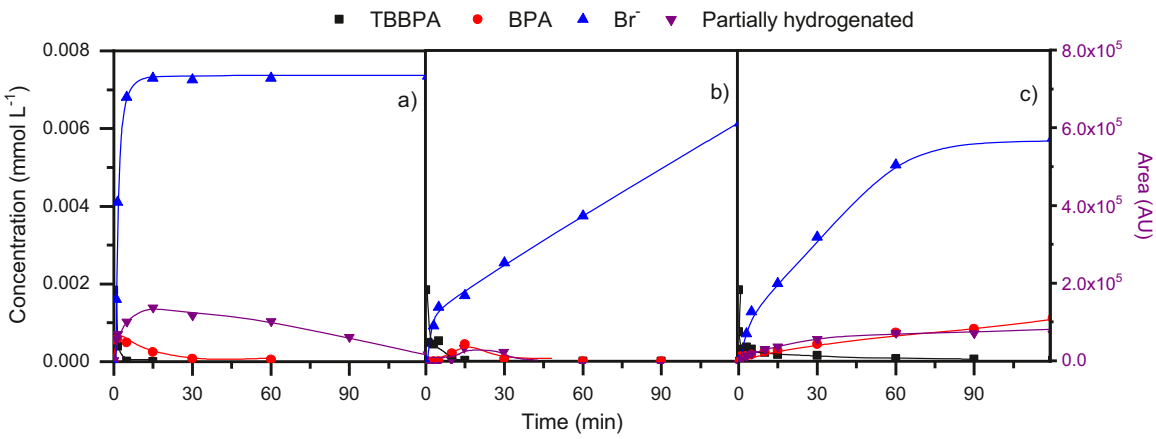


Fig. 2. Evolution of TBBPA and intermediates upon HDB with (a) Pd/Al_2O_3, (b) Rh/Al_2O_3 and (c) Pt/Al_2O_3 ($[TBBPA]_0$ = 1000 μg L^{-1}; H_2 = 50 N mL min^{-1}; $[Catalyst]_0$ = 1 g L^{-1}; 25 °C).

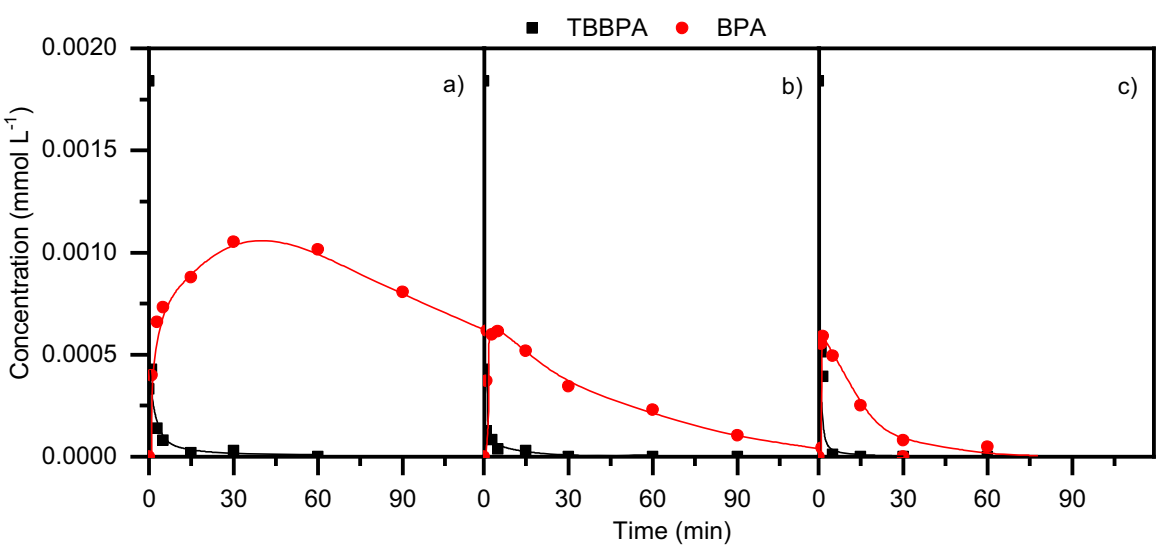


Fig. 3. Evolution of TBBPA and intermediates upon HDH with different Pd/Al_2O_3 catalyst load (a) 0.25 g L^{-1}, (b) 0.5 g L^{-1} and (c) 1 g L^{-1} ($[TBBPA]_0$ = 1000 μg L^{-1}; H_2 = 50 N mL min^{-1}; 25 °C).

water pollutants such pharmaceuticals given rise to the formation of organobrominated compounds [34]. Thus, the integration of HDH could be implemented as a potential polishing step in DWTPs.

4.4. Pd/Al_2O_3 catalyst stability

According to the literature, one of the main limitations of HDH technology is the catalyst deactivation due to hydrohalic acids poisoning, metal leaching or fouling by-products adsorption [35]. Considering the high cost of catalysts based on precious metals such as palladium, ensuring their stability for consecutive applications is crucial for the process feasibility. In this work, stability of the Pd/Al_2O_3 catalyst was evaluated upon three consecutive runs (see Fig. S9 of the Supplementary Material). Notably, the activity after the third run was close to those obtained with the fresh catalyst. TBBPA was completely degraded in short reaction times and BPA was completely hydrogenated at the end of all the cycles. Despite the strong adsorption of TBBPA at the beginning of reaction, carbonous deposits did not block the Pd active sites probably due to the complete reaction of the adsorbed TBBPA along the 2 h reaction time. In fact, bromine balance was closed above 95% in the three

sequential runs.

4.5. Kinetic model

Once demonstrated that the HDH process is effective for the removal of TBBPA in water matrices, a kinetic model was proposed based on the reaction pathway shown in Scheme 1. In this sense, the main steps of the process including the hydrodebromination step of TBBPA, bromine formation and BPA hydrogenation were considered. The HDH process takes place under kinetic control since the existence of internal and external mass transfer limitations can be discarded according to the experimental results obtained both in this work and in previous ones [26,33]. Furthermore, the catalyst concentration was kept constant and H_2 was in excess during HDH reaction. Taking all these aspects into account and considering pseudo-first order kinetic equations to describe the different reaction steps, the following kinetic model was proposed:

$$(r_{TBBPA}) = \frac{-dC_{TBBPA}}{dt} = k_1 \cdot C_{TBBPA} \quad (1)$$

$$(r_{BPA}) = \frac{dC_{BPA}}{dt} = k_2 \cdot C_{TBBPA} - k_3 \cdot C_{BPA} \quad (2)$$

$$\left(r_{Br-}\right) = \frac{dC_{Br-}}{dt} = 4 \cdot \left(\frac{-dC_{TBBPA}}{dt}\right) = 4 \cdot k_2 \cdot C_{TBBPA} \quad (3)$$

where C_{TBBPA}, C_{BPA} and C_{Br-} are the concentrations of TBBPA, BPA and Br^- in solution (mmol L^{-1}) and k_1, k_2 and k_3 are the apparent first-order rate constants. As has been aforementioned, hydrodebromination of both dissolved TBBPA and that adsorbed onto the catalyst occurs at the operating conditions used in this work and thus, k_2 rate constant is referred to the TBBPA from both vias. Integrating Eqs. (1)–(3) with the initial values $t = 0$, $C = C_{TBBPA_0}$ where C_{TBBPA_0} corresponds to the starting concentration of TBBPA, Eqs. (4)–(6) were obtained:

$$C_{TBBPA} = C_{TBBPA_0} \cdot \exp(-k_1 \cdot t) \quad (4)$$

$$C_{BPA} = \frac{k_2 \cdot C_{TBBPA_0}}{k_3 - k_2} \cdot (\exp(-k_2 \cdot t) - \exp(-k_3 \cdot t)) \quad (5)$$

$$C_{Br-} = 4 \cdot C_{TBBPA_0} \cdot (1 - \exp(-k_2 \cdot t) \quad (6)$$

The experimental data were simultaneously fitted by Eqs. (4)–(6) using the Software Origin 2018 with the Levenberg Marquardt algorithm at a 95% probability level. The starting TBBPA concentration calculated from the kinetic model (0.00,184 mmol L^{-1} (1000 μg L^{-1})) is in accordance with the initial concentration established in the experiments (1000 μg L^{-1}), showing that not only the TBBPA in solution but also TBBPA adsorbed on the catalyst at the begging reacted completely. The resulting kinetic rate constant values were 1.165, 0.431 and 0.385 min^{-1} for k_1, k_2 and k_3, respectively. The correlation coefficient was 0.99. As can be seen in Fig. 4, experimental data were successfully fitted by the proposed model. The kinetic rate constant k_1 corresponds to TBBPA disappearance including both HDH and TBBPA adsorption effects. k_2 lumps all debromination reactions, including TBBPA disappearance, therefore it can be also related to the appearance rate of bromide considering the stoichiometric coefficient (4 bromine atoms are produced for each molecule of TBBPA completely dibrominated). Meanwhile, k_3 which corresponds to the hydrogenation reaction of BPA, showed the lowest value. This fact suggest that Pd/Al_2O_3 is significantly more active for the hydrodebromination steps than for the hydrogenation ones.

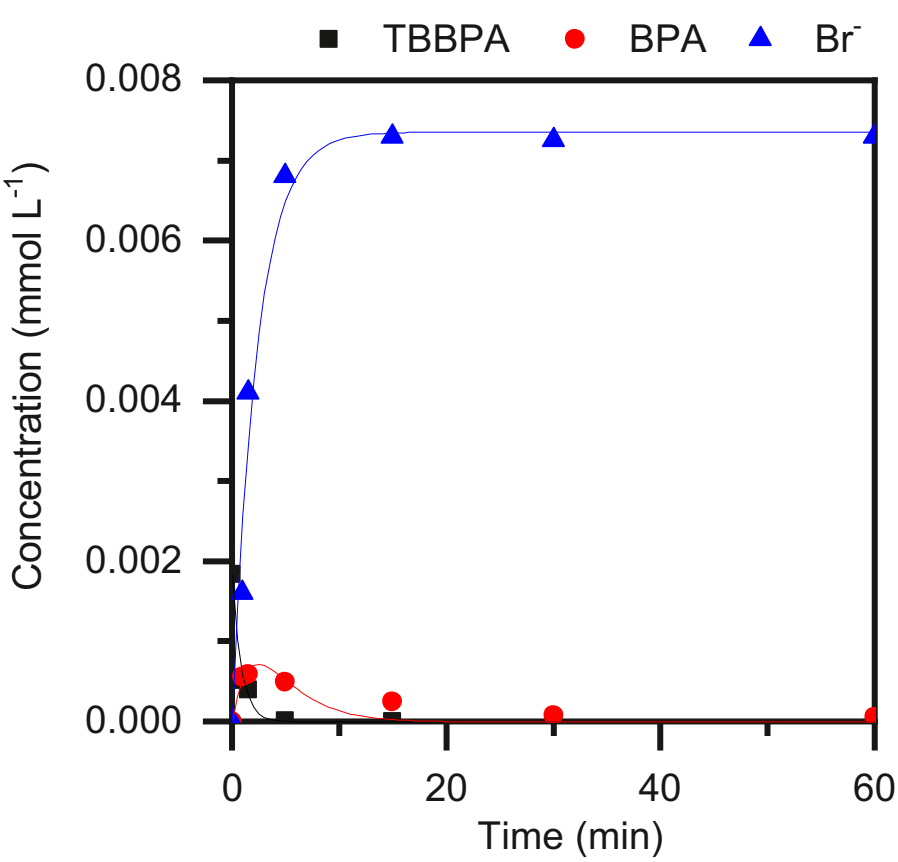
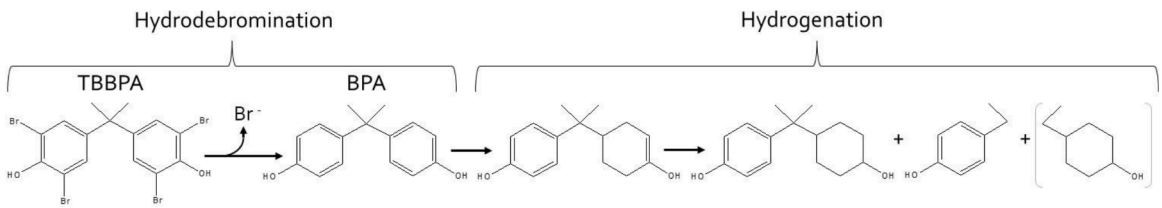


Fig. 4. HDH of TBBPA over Pd/Al_2O_3 ($[TBBPA]_0$ = 1000 μg L^{-1}; H_2 = 50 N mL min^{-1}; $[Pd/Al_2O_3]$ = 1 g L^{-1}; 25 °C). Experimental (symbols) and model fit (solid lines).



Scheme 1. Reaction pathway of TBBPA with Pd/Al_2O_3 catalyst.

5. Conclusions

The feasibility of HDH technology has been demonstrated for the removal of TBBPA, a brominated flame retardant that can led negative effects to the environment. The complete debromination of the pollutant was achieved in a short reaction time (< 5 min) under ambient conditions using the commercial Pd/Al_2O_3 catalyst, while Rh/Al_2O_3 and Pt/Al_2O_3 catalysts required longer times. The bromine-free BPA product, a well-known endocrine disruptor, was formed but it was further hydrogenated along reaction when Pd/Al_2O_3 is used as catalyst. Thus, a reaction pathway was proposed including both hydrodebromination and hydrogenation steps. Although TBBPA suffered a strong adsorption effect on the catalyst surface, the micropollutant reacted completely and bromine balance was closed (> 95%) using the Pd/Al_2O_3 catalyst. Moreover, a complete conditions study was carried out with the most promising catalyst (Pd/Al_2O_3). It was demonstrated that H_2 flow is not a limiting factor at the operating conditions tested in this work and external mass transfer limitations were discarded since degradation rates increased linearly with the catalyst load. In addition, an apparent activation energy of 36 kJ mol^{-1} was obtained. Remarkably, the catalytic system showed a reasonable stability upon three consecutive HDH applications. Finally, a kinetic model was developed, allowing to successfully describe all the experimental data.

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.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ceja.2021.100212.

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