



Combining efficiently catalytic hydrodechlorination and wet peroxide oxidation (HDC–CWPO) for the abatement of organochlorinated water pollutants



Macarena Munoz*, Zahara M. de Pedro, Jose A. Casas, Juan J. Rodriguez

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

ARTICLE INFO

Article history:

Received 28 September 2013
Received in revised form 5 December 2013
Accepted 16 December 2013
Available online 24 December 2013

Keywords:

Catalytic hydrodechlorination
Catalytic wet peroxide oxidation
Combination of HDC–CWPO
Chlorophenol

ABSTRACT

The combination of catalytic hydrodechlorination (HDC) and wet peroxide oxidation (CWPO) has been investigated for the breakdown of chlorophenols (CPs). The process was conducted as a sequential two-step reaction involving 30 min HDC followed by CWPO. Direct application of CWPO to CPs has shown important drawbacks derived from the formation of toxic intermediates under substoichiometric H_2O_2 doses as well as from the fact that the reaction rate decreases significantly as the number of chlorine atoms in the molecule increases (pseudo-first order rate constant values of 20.6×10^{-3} , 4.6×10^{-3} and $1.4 \times 10^{-3} \text{ L g}_{\text{cat}}^{-1} \text{ min}^{-1}$ were obtained for 4-CP, 2,4-DCP and 2,4,6-TCP disappearance, respectively). On the opposite, HDC removes chlorine from CPs under mild conditions at a frankly high rate which is almost unaffected by the chlorine content of the starting chlorophenol (values of 0.19, 0.17 and 0.15 $\text{L g}_{\text{cat}}^{-1} \text{ min}^{-1}$ for the pseudo-first order rate constants were obtained with 4-CP, 2,4-DCP and 2,4,6-TCP, respectively). Thus, HDC can be used as a short-time pretreatment (≈ 30 min) associated to a subsequent CWPO step in order to achieve a high mineralization in significantly lower reaction times. The sequential combination of HDC and CWPO as a two-step reaction was tested with different CPs using monometallic catalysts for each step ($\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$, respectively). This combined process allowed improving TOC reduction from 30% (CWPO alone) to 70% after 120 min reaction time. Moreover, it allowed reaching a substantial reduction of ecotoxicity (>95%) with the three chlorophenols tested.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The development and implementation of suitable treatments for industrial wastewater containing organochlorinated pollutants has attracted an increasing attention in the last two decades. Fenton oxidation is a well-established process to treat industrial wastewater due to its simplicity as well as its ability to degrade a wide variety of organic pollutants [1–4]. The use of solid catalysts in the so-called catalytic wet peroxide oxidation (CWPO) presents some important advantages respect to the conventional homogeneous Fenton process since the catalyst is not lost in the effluent, thus additionally avoiding the formation of iron sludge upon final neutralization step. Among the catalysts commonly used in CWPO, those based on iron supported on alumina have proved to be highly active and stable in the treatment of different organic pollutants [5–7].

Although CWPO has been widely applied for different persistent organic pollutants, the oxidation of organochlorinated compounds requires special attention. In recent works [8–10] it has been

demonstrated that partial oxidation of chlorophenols by Fenton oxidation under substoichiometric H_2O_2 doses leads to the formation of highly toxic condensation species such as chlorinated diphenyl ethers, biphenyls and dibenzofurans. On the other hand, the rate of oxidation of organochlorinated compounds by CWPO decreased significantly as the number of chlorine atoms of the molecule increased due to steric hindrance, which means that polychlorinated pollutants are highly resistant to oxidation [11,12].

Catalytic hydrodechlorination (HDC) appears as a potential emerging technology for the treatment of organochlorinated pollutants since it can be carried out at mild conditions, shows a low sensitivity to pollutants concentration and does not lead to more toxic chlorinated by-products [13,14]. In fact, this technology has been successfully applied with a wide variety of chlorine-containing organic compounds such as chlorophenols, chlorobenzenes, chlorodioxins, chlorodibenzofurans or chlorofluorocarbons [15,16]. Upon HDC organochlorinated compounds react with a source of hydrogen giving rise to HCl and the corresponding de-chlorinated species, which allows reducing substantially the ecotoxicity of the effluent. However, this process does not reduce the amount of total organic carbon (TOC) and thus, the exit stream needs further treatment in order to achieve a high abatement of the organic load.

* Corresponding author. Tel.: +34 91 497 3991; fax: +34 91 497 3516.
E-mail address: macarena.munoz@uam.es (M. Munoz).

The combination of HDC and CWPO has been scarcely studied and could represent an effective and environmentally friendly solution for the treatment of aqueous streams containing organochlorinated pollutants [17,18]. HDC can be used as a short-time pretreatment in order to remove the chlorine atoms from the organochlorinated pollutants followed by a CWPO step addressed to TOC reduction. In a recent contribution [18] we developed a bimetallic catalyst, based on Fe and Pd, capable of working efficiently for both HDC and CWPO. However, a significant deactivation was observed upon successive applications, which was attributed to Fe leaching due to the HCl produced upon HDC.

In order to overcome the drawbacks associated to the low stability of the bimetallic Pd–Fe catalyst, in this work the HDC and CWPO steps were carried out with monometallic catalysts of Pd and Fe, respectively, supported on γ -alumina in both cases. Three different chlorophenols were tested as target compounds: 4-chlorophenol (4-CP); 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP). Those chlorophenols have been widely used in the literature as representative of organochlorinated pollutants in industrial wastewater. They constitute a particular group of priority pollutants regarded by the EU [19] and US EPA [20] which can be found in a wide variety of industrial wastewater since they are used in the manufacture of a diversity of chemical products like pesticides, herbicides, germicides, fungicides and wood preservatives. First, an in-depth study of the CWPO of those three CPs was accomplished with an own-prepared Fe/ γ -Al₂O₃ catalyst. A wide range of H₂O₂ doses was covered in order to identify the by-products formed and follow the evolution of ecotoxicity under different oxidant loads. Secondly, the HDC study was carried out with a Pd/ γ -Al₂O₃ catalyst, also prepared in our lab. The kinetics of the process is analyzed on the basis of the reaction pathway proposed from the identification of by-products. Finally, the effective combination of HDC and CWPO was investigated and the stability of both catalysts (Pd/ γ -Al₂O₃, Fe/ γ -Al₂O₃) was tested in a long-term continuous HDC–CWPO experiment.

2. Materials and methods

2.1. Catalysts preparation and characterization

The catalysts used in this work (Fe/ γ -Al₂O₃; Pd/ γ -Al₂O₃) were prepared by incipient wetness impregnation of powdered γ -Al₂O₃ supplied by Merck (Germany). Aqueous solutions of Fe(NO₃)₃·9H₂O and PdCl₂ were used as precursors for the CWPO (Fe/ γ -Al₂O₃) and HDC (Pd/ γ -Al₂O₃) catalysts, respectively. The Fe and Pd loads were adjusted to 4% and 1% (w/w), respectively. After impregnation, the solids were left for 2 h at room temperature, dried for 12 h at 60 °C and calcined for 4 h at 300 °C [7]. An additional reduction in H₂ atmosphere was carried out for 2 h at 350 °C in the case of the Pd/ γ -Al₂O₃ catalyst.

The textural properties of the fresh and used catalysts were characterized from nitrogen adsorption–desorption isotherms at –196 °C using a Micromeritics Tristar 3020 apparatus. The samples were previously outgassed overnight at 150 °C to a residual pressure of <10^{–3} Torr. Total iron and palladium contents were measured by inductively coupled plasma (ICP/MS) with a ICP-MS Elan 6000 Perkin-Elmer Sciex. The carbon content of the used catalysts was determined by a LECO CHNS-932 Elemental Analyzer while the chlorine content was analyzed by total reflection X-ray fluorescence (TRXF), using a TXRF spectrometer 8030c. X-ray photoelectron spectroscopy (XPS) was used for surface analysis with a Thermo Scientific, model k-Alpha equipped with a K α X-ray excitation source, 1486.68 eV. Software “XPS-Peak” was employed for deconvolution of the XPS profiles. The superficial metal content was calculated from the area of the spectral peaks. Palladium

dispersion on the Pd/ γ -Al₂O₃ catalyst was determined from CO chemisorptions at room temperature in a Micromeritics Chemisorb 2750 automated system equipped with Chemisoft TPx software. Prior to chemisorption measurements, the samples were reduced in H₂ flow at 350 °C for 2 h. A 1:1 stoichiometry was taken for CO adsorption over the Pd atoms [21,22].

Characterization of the porous structure of the raw alumina and the synthesized Fe/ γ -Al₂O₃ and Pd/ γ -Al₂O₃ catalysts confirmed their mesoporous character since the BET and the external or non-microporous areas were almost coincident. Impregnation of the support did not practically affect the BET surface area (138 m² g^{–1} for γ -Al₂O₃ vs. 136 and 134 for the Fe/ γ -Al₂O₃ and Pd/ γ -Al₂O₃ catalysts, respectively). According to the ICP-MS analyses the Fe and Pd content of the fresh catalysts were close to the nominal 4% and 1% (w/w) (3.9% and 0.95%, respectively). The content of chlorine of the fresh catalyst (0.37) was determined by TXRF. This value is similar to those found in other Pd catalysts prepared from palladium chloride and no significant effect on the activity of the catalysts was detected in previous works [23–25].

The XPS analyses of the Pd/ γ -Al₂O₃ catalyst served to establish the relative concentration of zero valent (Pd⁰) and electrodeficient (Pdⁿ⁺) palladium species. According to previous works [26–28] both species are required for HDC of organochlorinated compounds. The Pdⁿ⁺/Pd⁰ ratio of the fresh catalyst obtained by XPS was around 0.7. On the other hand, the CO chemisorption measurements revealed a fairly high dispersion of the active phase (33%) with a mean particle diameter of 3.5 nm. The ratio of the superficial (XPS) to the total (ICP) Pd content of the catalyst was 0.69, which indicates a quite homogeneous distribution of the active phase onto the alumina particles.

2.2. Experimental procedure

Both, the HDC and CWPO experiments were conducted in a 500 mL jacketed glass batch reactor stirred at 700 rpm to avoid mass-transfer limitations. A catalyst concentration of 2 g L^{–1} was always used, in powdered form (dp <100 μ m). The HDC runs were carried out at 30 °C and H₂ was continuously passed at 50 N mL min^{–1}. The use of H₂ gas excess would not represent a drawback for HDC since the exit gas stream can be easily recycled to the reactor [29]. Mono-, di- and trichlorophenols were used as target pollutants at 200 mg L^{–1} initial concentration for 4-CP and 2,4-DCP and 100 mg L^{–1} for 2,4,6-TCP which can be considered representative in different industrial wastewater [30–32]. Those chlorophenols were also selected in order to study the effect of the chlorine content on the degradation rate upon CWPO and HDC. The Cl/Pd molar ratios corresponded to 8.4, 13.2 and 8.1 for 4-CP, 2,4-DCP and 2,4,6-TCP, respectively. The CWPO experiments were carried out at 50 °C, which according to the literature allows achieving a high efficiency of H₂O₂ consumption [3,33,34]. The initial pH value of the reaction medium was adjusted to 3 with nitric acid and the H₂O₂ dose corresponded always to the theoretical stoichiometric amount for complete mineralization. A previous set of CWPO experiments were performed at high initial concentrations of chlorophenols (2000 mg L^{–1}) in order to better identify the reaction by-products. In this case, different H₂O₂ doses were used, covering from 20% to 100% of the theoretical stoichiometric amount for complete conversion of CPs into CO₂, H₂O and HCl.

The combination of HDC and CWPO was carried out as a sequential two-step reaction involving 30 min HDC followed by CWPO. The stability of the catalysts was tested in a HDC–CWPO sequential treatment in long-term continuous experiments using two stirred tank reactors in series. The effluent from the HDC stage was directly fed to the second tank where CWPO was accomplished.

Three replicates of each experiment were carried out. The data reproducibility was better than $\pm 5\%$ in all the cases. Preliminary

Download English Version:

<https://daneshyari.com/en/article/45924>

Download Persian Version:

<https://daneshyari.com/article/45924>

[Daneshyari.com](https://daneshyari.com)