

Hydrodechlorination of alachlor in water using Pd, Ni and Cu catalysts supported on activated carbon

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Abstract

The hydrodechlorination of alachlor with hydrogen in aqueous phase was studied in a trickle bed reactor using different activated carbon-supported catalysts. The reactor was continuously fed with a 50 mg/L solution of alachlor in water and a H₂/N₂ gas stream. The variables studied were space-time (44.8–448.3 kg_{cat} h/mol), H₂:N₂ volumetric ratio in the gas phase (1:1–1:4), temperature (308–373 K) and pressure (0.24–0.6 MPa). The results of the hydrodechlorination experiments were evaluated in terms of alachlor conversion and ecotoxicity of the exit stream. High conversion values and important reductions of ecotoxicity were obtained working under mild conditions of temperature (323–348 K) and pressure (0.24 MPa). Palladium catalysts supported on activated carbon were found as the most active in the hydrodechlorination of alachlor, although copper and nickel catalysts led also to high conversions in the 80–93% range. The hydrodechlorination of alachlor was performed successfully with metal loads between 0.5 and 2.5 wt.% on the catalysts. A significant metal leaching was observed from the nickel and copper catalysts, which negatively affected the ecotoxicity of the final effluents. Oxidative treatment of the activated carbon supports with nitric acid previous to the impregnation with the metal precursor improved the anchorage of the active phase and reduced leaching dramatically. Likewise, the activity was not influenced by the oxidation of the supports and reductions of ecotoxicity by more than 90% were observed.

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1. Introduction

The widespread use of fitosanitary products for agricultural and non-agricultural purposes has resulted in the presence of their residues in both surface and ground waters. Pesticides can reach the aquatic environment through direct run-off from crops, leaching, careless disposal of empty containers, equipment washing, etc. [1]. Due to the variability and multiplicity of origins of this pollution the problem becomes difficult to control. Moreover, the toxicity, stability to natural degradation and persistence in the environment of these compounds have been the causes of much concern to the societies and the regulatory authorities around the world. In this sense, the legislation has been constantly adapted to protect and improve the quality of water resources, and some water-soluble fitosanitary products have been designated as priority pollutants.

Compounds such as alachlor, atrazine, chlorofenvinfos, diuron, isoproturon and pentachlorophenol have been detected in surface and ground waters and have the potential to reach the levels that exceed the health-based standards. Special attention has been paid to alachlor, a chlorinated aniline herbicide of widespread use for pre-emergent weed control in corn, soybeans and peanuts crops. Undesirable side effects such as toxicity and carcinogenicity confer to it the character of hazardous pollutant whose presence in water has to be carefully controlled [2].

A number of processes and technologies are available for the treatment of water-containing fitosanitary products. Physical and physico-chemical techniques (coagulation, adsorption on activated carbon, reverse osmosis, etc.) can be used for the removal of such pollutants. These methods are non-destructive and post-treatment and/or careful disposal of the spent adsorbent or the solid wastes generated become necessary, thus substantially increasing the treatment costs. Biological treatments are adopted in many cases as the best available technology for the elimination of organic pollutants, but they are not appropriate when the wastewaters contain recalcitrant toxic contaminants.

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Implementation of cost-effective technologies is needed for a suitable treatment of ground and surface waters polluted with fitosanitary products. The application of oxidative treatments such as advanced oxidation processes (AOPs) has received a significant attention in the last years, since a number of these techniques ($\text{H}_2\text{O}_2 + \text{UV}$, $\text{O}_3 + \text{UV}$, $\text{H}_2\text{O}_2 + \text{O}_3$, photo-Fenton, $\text{TiO}_2\text{-UV}$, etc.) can convert those compounds to less harmful biodegradable species [3]. Farre et al. [4] studied both homogeneous and heterogeneous photocatalytic ozonation for the degradation of biorecalcitrant fitosanitary products such as alachlor, atrazine, clorofenvinfos, diuron, isoproturon and pentachlorophenol. The best results in terms of TOC reduction and detoxification were obtained by means of photo-Fenton/ O_3 treatment, except in the case of atrazine and alachlor. Some economic studies on the application of AOPs have concluded that the research interest should focus mainly on those techniques that can be driven by solar radiation (wavelength above 300 nm) such as photo-Fenton and heterogeneous catalysis with UV/ TiO_2 [3,5,6]. Thus, Hincapie et al. [7] have studied the degradation of alachlor, atrazine and diuron with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, TiO_2 and $\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$ treatments driven by solar energy using a compound parabolic collector photoreactor. Photo-Fenton using iron at low concentration was found to be efficient for treating aqueous solutions of these fitosanitary products giving rise to a high TOC reduction. Nevertheless, the neutralization of the treated effluent (pH 3), the cost of hydrogen peroxide and a relatively low reaction rate are some factors that must be carefully analyzed before considering the implementation of this treatment.

An alternative approach for the treatment of chlorinated fitosanitary products is catalytic hydrodechlorination. The catalytic hydrogenolysis of organochlorine compounds is a viable, low cost and environmentally friendly methodology which has been applied to different types of chlorinated compounds such as polychlorinated benzenes, chlorophenols, halogenated hydrocarbons, PCBs, dioxins, etc., leading to their conversion into much less harmful substances [8]. This process shows some advantages with regard to other methods for the elimination of chlorinated organics. It can be adapted to wastewaters with a wide range of concentrations, permits to work at mild conditions (pressure and temperature) and the selectivity towards the different reaction products can be controlled through the selection of an adequate catalyst [9–11].

A number of catalysts have been proposed for liquid-phase hydrodechlorination, being carbon-supported catalysts among the most active. They have some advantages such as the relatively low cost of the supports which have a high surface area, the possibility of easy recovery of the supported metal by simple combustion of the support, and good chemical stability [12]. In the case of metallic active phases supported on activated carbon, the surface chemistry plays an important role on the metal dispersion and the catalytic behavior. The surface chemistry can be modified through thermal and/or oxidative treatments which may lead to an increase in the amount of surface oxygen complexes [13]. The most widely used active phases are noble metals such as palladium, platinum, rhodium

and ruthenium, although transition metals have also received attention due to their lower cost and the resistance to corrosion of Ni-based catalysts [14]. Transition metals catalysts have been mainly used supported on alumina, silica or zeolites for hydrodechlorination reactions [15]. Nevertheless, there is so far a scarce literature on hydrodechlorination with copper and nickel catalysts supported on activated carbon. Previous works in literature [14,16,17] only reported the use of nickel and copper in low proportions in bimetallic catalysts. In this work, we report our results on the hydrodechlorination of alachlor using different carbon-supported copper, nickel and palladium catalysts. The efficiency of this treatment was evaluated not only for the herbicide elimination, but also reduction of ecotoxicity.

2. Experimental

2.1. Preparation and characterization of the catalysts

A 0.5 wt.% commercial palladium on activated carbon (Pd/AC) catalyst supplied by Engelhard and different own-made catalysts prepared by wetness incipient impregnation were tested. The catalyst particle size used in the hydrodechlorination experiments was between 1 and 2 mm. The activated carbons used as supports were supplied by Merck (Mk) and Chemviron (Ch). As active phases were used palladium, copper and nickel with a nominal loading of 0.5, 0.5–5 and 0.5–10 wt.%, respectively. The precursor salts employed were PdCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$. Impregnation was followed by drying at room temperature for 2 h and overnight at 333 K. Finally, the catalysts were calcined at 473 K and reduced in H_2 atmosphere at 373 K with a flow rate of 60 N mL/min. In some cases, the activated carbon support was subjected to an oxidative treatment with HNO_3 prior to impregnation. Oxidation was carried out by boiling 1 g of activated carbon in 10 mL of 6 N aqueous HNO_3 solution for 20 min [18]. The nomenclature used for the catalysts is shown in Table 1.

The porous structure of the activated carbons and the catalysts was characterized by N_2 adsorption–desorption at 77 K (Autosorb-1 Quantachrome). The BET equation was used to obtain the surface area and the t -method for the micropore volume. The external or non-micropore surface area was also obtained from the t -method. The difference between the volume of N_2 adsorbed at 0.95 relative pressure (calculated as liquid) and the micropore volume was taken as the mesopore volume. The catalysts were analyzed by X-ray photoelectron spectroscopy (XPS), using a Physical Electronics model 5700 apparatus with a Mg $\text{K}\alpha$ X-ray excitation source (1253.6 eV), to determine palladium, copper and nickel concentration.

2.2. Experimental set-up and procedure

The hydrodechlorination experiments were carried out in a trickle bed reactor (9 mm i.d. stainless steel tube) with concurrent downflow of both phases, liquid and gas (Fig. 1). Mass flow controllers were used to prepare different hydrogen/

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