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Detoxification of Kraft pulp ECF bleaching effluents by catalytic hydrotreatment

L. Calvo*, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodríguez

Sección de Ingeniería Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

Two different effluents from the D_1 and E_1 stages of the ECF bleaching of *Eucalyptus globulus* kraft pulp were treated by catalytic hydrogenation in a trickle bed reactor using commercial and homemade Pd/AC catalysts. The reactor was fed with the bleaching effluent and a H_2/N_2 gas stream. The variables studied were space-time (1.4–5 g_{cat} min/mL), gas to liquid flow ratio (286–1000 vol.), gas feed concentration (H_2:N_2, 1:1–1:7.3 vol.), temperature (25–100 °C) and pressure (1–11 bar). Hydrotreatment performance was evaluated in terms of ecotoxicity, adsorbable organic halogen (AOX), chemical oxygen demand (COD), biological oxygen demand (BOD_5) and colour removal. In all the runs, the ecotoxicity of the effluents decreased as a result of the treatment, achieving reductions that ranged from 70% to 98%. Simultaneously to the reduction of toxicity, the hydrotreatment led to a decrease of the colour of the effluents, being the decrease significantly higher in the case of E_1 effluent. The AOX content was reduced by 85% and 23% for E_1 and D_1 effluents, respectively. In the case of D_1 effluent the removal of ecotoxicity was significantly higher than that of AOX, which indicates that much of the toxicity of the effluent must be associated to non-chlorinated organics. In spite of the important reduction of ecotoxicity, the biodegradability of the effluents only increased slightly. The homemade catalysts, prepared from activated carbons with a high external or non-microporous surface area and mesopore volume and a convenient surface chemistry showed a higher efficiency than the commercial one.

1. Introduction

Water pollution is a major concern for the pulp and paper industry due to the large quantities of effluents generated. The effluents from pulp bleaching are responsible for most of the colour, organic matter and toxicity of the water discharges of this industry. Two main approaches have been used to comply with pollution control regulations: in-plant modifications, such as extended delignification or substitution of chlorine-based bleaching processes, and the treatment of effluents by physicochemical and biological methods (Torrades et al., 2003).

The use of chlorine gas and hypochlorite as bleaching chemicals was a common practise until the mid-1980s. At this time the identification of polychlorinated dioxins, furans and other toxic organics led to the development of new bleaching sequences where elemental chlorine was substituted by chlorine dioxide and/or hydrogen peroxide, ozone and enzymes, which gave rise to elemental chlorine-free (ECF) and totally chlorine-free (TCF) bleaching (Ali and Sreekrishnan, 2001). In spite of the interest of the elimination of chlorine-based chemicals in bleaching operations, the control of TCF bleaching is difficult and pulps with lower strength and brightness are obtained. Thus, TCF pulp only maintains a

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*Corresponding author. Tel.: +34 914978774; fax: +34 914973516.
E-mail address: luisa.calvo@uam.es (L. Calvo).

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small niche market around 5% of the world bleached chemical pulp production, being mainly sold and used in Germany (Pryke, 2003). On the opposite, ECF bleaching has become the world standard for chemical pulp bleaching accounting for more than 75% of all chemically produced pulp and has displaced gradually chlorine bleaching. This trend is expected to continue at least at medium term.

The $D_0E_1D_1E_2D_2$ sequence can be considered as representative of conventional ECF bleaching (Pinto et al., 2005), where D stands for chlorine dioxide oxidation stage at acidic conditions and E for an alkaline extraction with aqueous sodium hydroxide. Chlorine dioxide causes lignin cleavage and the oxidation of lignin fragments giving rise to hydrophilic carboxylic groups. These combined actions increase the overall solubility of lignin (Sjöström, 1993). During the reaction between chlorine dioxide and lignin some chlorine is formed, which is responsible for part of the bleaching and much of the generation of chlorinated organics. As a common practise the E_2 effluent is reused in the E_1 stage and the D_2 effluent is sent to the D_1 stage. The majority of the chlorinated organics formed are thus contained in the effluent from the E_1 and D_1 stages. As a result, these effluents have strong colour and chemical oxygen demand (COD) (Ali and Sreekrishnan, 2001), likewise they contain variable amounts of chlorinated organics (Torrades et al., 2003).

The ECF bleaching effluents are considered less environmentally friendly than the TCF effluents since they contain chlorinated organics, although it has been shown that there are no important differences of toxicity between them, being the natural constituents of wood probably responsible for some of the toxicity of these bleaching effluents (Verta et al., 1996). To assess the hazards associated to ECF bleaching effluents it must also be taken into account that chlorinated organics are acute or even chronic toxins and that they can induce genetic defects and cancer in exposed organisms (Ali and Sreekrishnan, 2001). Chlorinated organics also show an inhibitory effect to microbes in conventional biological treatments (Vidal et al., 1997), which in addition to the low biodegradability of lignin fragments leads to a low efficiency of conventional biological processes (Xie et al., 2005; Ali and Sreekrishnan, 2001; Peralta-Zamora et al., 2004). Thus, in biological systems the typical removal efficiencies of COD and adsorbable organic halogens (AOX) show values of 35–70% and 25–55%, respectively (Tezel et al., 2001).

Due to the limitations of biological treatments, a variety of physical and chemical processes have been proposed for the treatment of bleaching effluents, including coagulation, precipitation, ultrafiltration, reverse osmosis, ion exchange, freezing, electrolysis and catalytic oxidation (Chen et al., 2003). However, only biological treatment, coagulation and precipitation have been implemented in industrial practise.

The application of oxidative treatments to bleaching effluents has received a significant attention in the last years. Pintar et al. (2001a, b, 2004) have shown that wet air oxidation (WAO) can provide a reduction of 99% or higher of the TOC of bleaching effluents at 463 K and 5.5 MPa when ruthenium catalyst supported on titanium and zirconium oxides are used in a slurry batch reactor. Thus, almost complete mineralization to CO_2 (only trace amounts of acetic acid were found) was achieved. Equivalent removal efficiencies were found for a trickle bed reactor.

A variety of advanced oxidation processes (AOPs) have also been tested with good results regarding to removal of COD and AOX from bleaching effluents. The combination of Fenton and photo-Fenton oxidation showed an efficiency over 95% in the removal of TOC when carried out at optimal conditions (Pérez, 2002a; Torrades et al., 2003). Likewise, Fenton, Fenton-like and photo-Fenton processes were found to be efficient in the elimination of chlorophenolic compounds. Ozone treatment has been reported to yield a significant TOC removal, especially under UV light irradiation (Pérez, 2002a; Muñoz et al., 2006). Wang et al. (2004) have also shown that when the ozone treatment is combined with UV light irradiation the removal of AOX increases, but the reduction of colour is lower than that obtained with ozone alone. Photocatalysis with titanium dioxide showed a rather low yield (around 50–75%) in the reduction of COD and TOC when compared to other AOPs (Balcioglu and Arslan, 1998; Yeber et al., 2000; Pérez et al., 2001; Machado et al., 2003); however, the selectivity towards AOX destruction was significant and more than 90% of these compounds were removed, which enabled a drastic reduction of the toxicity of the effluent. Photocatalysis with titanium dioxide has also been combined with hydrogen peroxide, leading to enhanced removal of COD and an improvement in the reduction of colour carriers, while the degradation of chlorinated compounds was not effective (Pérez et al., 2001).

Economic studies on the application of AOPs have indicated that the best choice is to balance the efficiency in terms of pollutants removal with the cost of the process (Pérez, 2002b). Besides, Muñoz et al. (2006) have recently applied life cycle assessment for the evaluation of different AOPs applied to the removal of organic mater from Kraft pulp bleaching effluents showing that some AOPs are so energy intensive that the energy consumption produces an important environmental impact in addition to the associated cost. These results show the interest for the development of treatment processes that can be operated at mild conditions. In this sense, catalytic hydrodechlorination can be an interesting alternative/complement for the elimination of chlorinated organics. In previous works it was shown that chlorophenols bearing effluents can be successfully treated at 50–75 °C and 2–3 bar, providing a removal efficiency over 99% together with a reduction of ecotoxicity higher than 96% (Calvo et al., 2004, 2005, 2006). Since chlorinated phenolics are among the main xenobiotics generated during ECF bleaching, hydrodechlorination appears, in principle, as an interesting alternative technique for its application to the treatment of bleaching effluents. Hydrodechlorination does not allow COD removal, but it could be coupled to a biological system as a pretreatment to reduce the toxicity and improve biodegradation. This work deals with the study of catalytic hydrotreatment of ECF effluents from the E_1 and D_1 stages using Pd/activated carbon (Pd/AC) catalysts with the aim of reducing the toxicity of that type of wastewaters.