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Treatment of a non-azo dye aqueous solution by CWAO in continuous reactor using a Ni catalyst derived from hydrotalcite-like precursor

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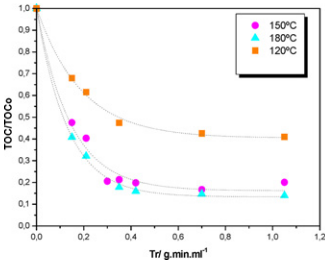
HIGHLIGHTS

- ▶ Ni supported over hydrotalcite calcined precursors as catalyst.
- ▶ Catalytic wet air oxidation in trickle bed reactor for Basic Yellow 11 removal.
- ▶ Dye removal depends on temperature, initial dye concentration and flow rate.
- ▶ The catalyst proved to be stable and efficient for the dye degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic wet air oxidation (CWAO) of a Basic Yellow 11 (BY11) aqueous solution, chosen as a model of a hardly biodegradable non-azo dye was carried out in a continuous-flow trickle-bed reactor, using nickel supported over hydrotalcite precursor calcined at 550 °C. An increase in the reaction temperature (120–180 °C), and a decrease in dye concentration (1000–3000 ppm) or liquid flow rate (0.1–0.7 mL min^{-1}) enhanced the CWAO performance in a 30 and 19% for the variation of the temperature and concentration respectively. After a small leaching observed within the first hours, the catalyst proved to be very stable during the 65-day reaction. The CWAO process was found to be very efficient, achieving BY11 conversion up to 95% and TOC conversion up to 85% at 0.1 mL min^{-1} and 180 °C under 5 MPa air.

1. Introduction

Wastewater produced in many industrial processes often contains organic compounds that are toxic and not amenable to direct biological treatment. Among these, wastewaters from textile, dyeing and graphic arts industry may cause severe environmental problems. It is reported that almost 20% of dyes are not fixed and are lost in wastewater during the dyeing process [1]. These effluents are characterized by strong color, high level of Total Organic Carbon (TOC) and low biodegradability. Furthermore, these chemicals may present a toxic, carcinogenic, mutagenic or teratogenic nature [2]. Therefore, these effluents must be treated before their discharge and have to achieve the standards required by the legislation [3,4].

New technologies have been developed and evaluated to degrade these pollutants, mainly based on chemical oxidations by Advanced Oxidation Processes (AOPs) such as O_3 [5], UV/O_3 [6], UV/H_2O_2 [7], photo Fenton [8] or wet air oxidation (WAO). WAO consists in the oxidation of the pollutants at high temperatures and pressures (175–320 °C, 0.5–20 MPa). This technology has already been applied successfully to treat effluents containing a large range of products, in particular from textile bleaching, printing and dyeing industries [9,10]. However, the performances

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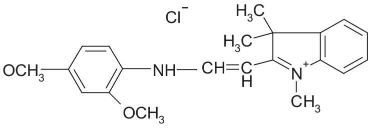
Table 1
Main characteristics and structure of Basic Yellow 11.

Dye	Structure	C.I. number	Molecular weight ($g\,mol^{-1}$)	Molecular formulae	λ_{max} (nm)
Basic Yellow 11		48,055	372.89	$C_{21}H_{25}ClN_2O_2$	413

of the WAO process may be strongly improved if a solid catalyst is employed (CWAO). The degradation of organic pollutants is then increased and milder conditions of temperature and pressure may be used [9,11]. It has been found [12] that the dye and TOC removal rates of several mono, di, and tri-azo dyes (Chromotrop 2R, Erionyl Red B and Solophenyl Green BLE) were significantly enhanced with respect to the non-catalytic reaction by using platinum supported on multi-walled nanotubes. CuO for dyeing and printing wastewater [13], $CoAl/PO_4{}^{-5}$ and CeO_2 for a reactive dyeing solution [14], Fe_2O_3–CeO_2–TiO_2/γ-Al_2O_3 for methyl orange azodye [15], polyoxotungstates for Acid Orange azodye [16], ZnO/MoO_3 for Safranin-T azine dye [17], and Cu/carbon nanofibers for different azo dyes [18] have been successfully examined as catalysts.

Non-azo dyes have been much less studied in the literature than azo dyes. Recently, the CWAO of the triaryl methane Crystal Violet dye has been studied in the presence of a Ni-hydrotalcite like catalyst in batch recycling experiments [19]. In the present work, the degradation of the Basic Yellow 11 (BY11) was studied, using the same HTNi catalyst. This particular non-azo dye was selected because it is hardly biodegradable by the conventional biological processes, but widely used in the textile, color solvent, ink, paint, paper, and plastic industries. Interest in hydrotalcites (HT) and derived materials arise from their relative ease of preparation and broad use as catalysts, catalysts supports, ion exchangers, stabilizers and adsorbents [20]. Ni catalysts derived from hydrotalcite-like precursors have shown remarkable properties such as high metal dispersion and stability against sintering, even under extreme conditions [21].

Since the stability and durability of a catalyst is a critical step in the implementation of this technology due to the severe conditions of pressure and temperature of the CWAO process [22,23] the study was first carried out in a batch reactor and then in a continuous-flow trickle-bed reactor. The catalyst efficiency was determined by the color degradation, TOC removal and total nitrogen (TN) removal.

2. Materials and methods

2.1. Materials and synthesis of catalysts

The dye was purchased from Sigma–Aldrich (Steinheim, Germany) and used without further purification (dye purity 40%). The main characteristics of this dye and its structure are shown in Table 1.

The hydrotalcite precursor was prepared by coprecipitation as described by Ovejero et al. [19]. $Mg(NO_3)_2{\cdot}6H_2O$ (0.05 mol) and $Al(NO_3)_2{\cdot}9H_2O$ (0.01 mol) (Sigma–Aldrich) dissolved in 100 mL of water to form solution A. Besides, Na_2CO_3 (0.03 mol) and NaOH (0.07 mol) were mixed in 60 mL of water to form solution B. Solution B was stirred for 1 h at constant temperature of 65 °C and then solution A was slowly dropped. The solution containing the precipitates was aged at 60 °C for 18 h. Then, the precipitates were filtrated and washed with distilled water at 40 °C for 2 h and dried at 100 °C for 12 h. Two particle sizes (0.125 and 0.5 mm) were obtained by sieving the dried hydrotalcite depending whether they are going to be employed in the batch (0.4 $g_{catalyst}$/100 mL) or trickle bed reactor (1.4 $g_{catalyst}$) respectively. Nickel was added by incipient wetness impregnation of the dried hydrotalcite precursor with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (Panreac, Barcelona, Spain). The precursor amount was calculated to obtain a 7 wt.% of nickel in the final material. Catalysts containing this loading have been proved to be the most efficient and stable in batch reactions for the CWAO of different dyes [24]. Finally, the resulting solids were calcined at 550 °C for 5 h (HTNi).

2.2. Characterization of catalysts

The support and the HTNi catalyst were characterized by physical adsorption of nitrogen at −196 °C in a Micromeritics ASAP 2010 apparatus. XRD patterns were recorded using a SIEMENS D-501 diffractometer. The metal loading was determined by means of X-Ray Fluorescence (XRF) (Broker S4 Explorer). More detailed characterization procedures can be found in previous work [19].

2.3. CWAO experiments

Experiments in batch mode were conducted in a 300 mL Hastelloy C22 high-pressure reactor. The reactor was equipped with an electrically heated jacket, a turbine agitator and a variable speed magnetic drive. The selected reaction temperature, pressure, and agitation speed was 180 °C, 5 MPa, and 1000 rpm, respectively. The choice of these values attends to the results found in previous studies [18,19]. The temperature and the stirring speed were controlled by means of a PID controller. The gas inlet, gas release valve, pressure gauge, rupture disk, and cooling water feed line were situated on the top of the reaction vessel. The liquid sampling line and the thermocouple well were immersed in the reaction mixture. The reactor was loaded with 100 mL of an aqueous solution of commercial dye without or with the catalyst (0.4 g). After flushing with argon, the system was heated to the desired temperature and a sample was withdrawn. TOC conversion during this heating period was negligible and this was considered as zero time for the reaction. Air from the cylinder was then introduced into the reactor and samples were withdrawn periodically after sufficient flushing of the sampling line. Pressure drop was monitored and additional air was charged in order to maintain a constant total pressure during each test. To check the BY11 adsorption on the catalyst a control experiment was run following the previous procedure but employing N_2 instead of air and argon during the reaction.

Continuous experiments were performed in a laboratory-scale, high-pressure fixed-bed reactor with co-current down-flow of gas and liquid phases. The equipment consists of a tube made of Hastelloy C (15 cm height and 1 cm i.d.) that was heated via a tubular furnace. The liquid feed was introduced from a glass tank into the system by means of an HPLC positive alternative displacement pump. Air was used as oxidant. Gas flow rate and pressure were adjusted with a back-pressure controller. The temperature