Chemical Engineering Journal 215–216 (2013) 168–173

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Catalytic wet air oxidation of a non-azo dye with Ni/MgAlO catalyst

Gabriel Ovejero, Araceli Rodríguez, Ana Vallet, Juan García *

Grupo de Catálisis y Procesos de Separación (CyPS), Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

HIGHLIGHTS

- Ni supported over hydrotalcite calcined precursors as catalyst.
- Catalytic wet air oxidation in batch reactor for Basic Yellow 11 removal.
- Effects of reaction conditions and catalyst stability were tested.
- The catalyst proved to be stable and efficient for the dye degradation.

ARTICLE INFO

Article history:
Received 18 July 2012
Received in revised form 15 October 2012
Accepted 6 November 2012
Available online 12 November 2012

Keywords:
Catalyst
CWAO
Dye
Hydrotalcite
Nickel

ABSTRACT

The catalytic activity of Ni supported over hydrotalcite by impregnation (Ni/MgAlO) as catalyst for Basic Yellow 11 (BY11) degradation under moderate conditions was investigated. BET, XRD and XRF were employed to characterize the catalyst. To evaluate the catalytic system, wet air oxidation of dye was carried out at temperatures between 100 and 200 °C, and oxygen pressures ranging from 30 to 60 bar. The effect of initial concentration from 100 to 400 ppm on the degradation of Basic Yellow 11 was also investigated. The degradation process was monitored by UV–VIS spectroscopy, TOC and toxicity analyses. At 150 °C, 50 bar oxygen pressure and 200 ppm initial concentration, 64.5% selectivity towards CO_2 was obtained after 3 h of treatment, while only 20.2% selectivity was achieved without catalyst at the same experimental conditions. The structure and morphology of the catalyst under different cycling runs show that the catalyst is stable under such operating conditions and the leaching tests show low leaching effect.

1. Introduction

Effluents from the dying and textile industry are considered one of the most problematic wastewaters and its disposal has become a major environmental problem. Those wastewaters are characterized by the presence of color, high total organic carbon (TOC) levels as well as an important chemical oxygen demand; mainly due to the presence of dyes and other organic by-products. Dye containing wastewaters are usually recalcitrant to degradation by the conventional biological treatments due to its high toxicity, as these compounds are often hardly biodegradable or even biocides. As a consequence, those effluents should be remediated by means of physicochemical technologies before its discharge or a biological treatment.

Nowadays, some physical operations [1] are available for the removal of organic pollutants from contaminated water, especially adsorption methods [2,3]. However, these techniques only allow the removal of pollutants, not its destruction, and additionally, generate large amounts of sludge [4,5].

Advanced Oxidation Processes (AOPs) are a promising alternative for wastewater treatment as they can provide complete mineralization of organic pollutants [6]. Among AOPs, wet air oxidation (WAO) is an attractive technique for industrial wastewater treatment. WAO involves the combustion of pressurized organic matter at relatively high temperatures. The main drawback of this technique is its high energetic requirements [6]. In order to be able to employ milder operating conditions and reduce the operating costs, catalytic wet air oxidation processes (CWAO) have been developed [7,8]. The presence of a catalyst may improve the overall reaction rate and enhances the removal of reaction intermediates compounds, which are refractory to the WAO process [9], improving the formation of hydroxyl radicals, well-known promoters of the oxidation [10].

Hydrotalcites (HTs) are anionic clays with a layered structure with high similarity to the Brucite, where cations Mg^{2+} have been

---

Abbreviations: WAO, wet air oxidation; CWAO, catalytic wet air oxidation; BY11, Basic Yellow 11; TOC, total organic carbon; TN, total nitrogen; TU, Toxicity Units; S_{NOC}, selectivity towards nonorganic compounds; X_{TOC}, TOC conversion; X_{dye}, dye conversion.

* Corresponding author. Tel.: +34 91 394 5207; fax: +34 91 394 4114.
E-mail address: juangcia@quim.ucm.es (J. García).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.11.028

partially substituted by Al^{3+} generating a positive charge in each layer which needs to be compensated by the introduction of anionic compounds in the interlayer space. These materials have received an increasing interest in recent years due to the number of potential applications in various fields such as catalysis, adsorption, medicine, and electro applications [11]. A large number of HT-like compounds have been extensively studied as catalyst precursors, since they show good dispersion values for the metal catalyst. Ni–Al–Mg mixed oxides, obtained from the calcination of nickel containing HT-like compounds, have shown remarkable properties as catalysts precursors such as high metal dispersion and stability against sintering, even under extreme conditions [11–14].

Non-azo dyes have been much less studied in the literature than azo dyes. Recently, the CWAO of the triaryl methane dye, Crystal Violet, has been studied in the presence of a Ni–hydrotalcite like catalyst in batch experiments [12]. In the present work, the degradation of the Basic Yellow 11 (BY11) was studied using the same catalyst. This particular non-azo dye has been selected as it is hardly biodegradable by the conventional biological treatments, but has also a wide use in a high number of industries, such as textile, paint, ink, paper and plastic ones.

The main objective of this work was to investigate the wet air oxidation of Basic Yellow 11 on aqueous solution employing Ni/MgAlO as catalyst. The influence of the temperature, initial concentration of dye, catalyst and pressure on dye removal was analyzed in detail. The catalyst efficiency was determined by the color degradation, TOC removal and toxicity reduction. Additionally, the reuse of the catalyst was also examined.

2. Materials and methods

2.1. Materials and catalyst synthesis

The dye was purchased from Sigma–Aldrich (Steinheim, Germany) and employed without further purification (dye purity 40%). The principal characteristics of BY11 can be seen in Table 1.

The hydrotalcite precursor was prepared by coprecipitation as described by Ovejero et al. [12]. $Mg(NO_3)_2 \cdot 6H_2O$ (0.05 mol) and $Al(NO_3)_2 \cdot 9H_2O$ (0.01 mol) were mixed in 100 ml of deionized water to obtain solution A. Besides, Na_2CO_3 (0.03 mol) and NaOH (0.07 mol) were dissolved in 60 mL of deionized water to form solution B. All the reactants were provided by Sigma–Aldrich. Solution B was stirred for 1 h at constant temperature of 65 °C and once this solution has reached the desired temperature (65 °C), solution A is slowly dropped, forming a white precipitate. The resulting precipitates were aged at 60 °C during 18 h in order to allow the formation of the HT structure. Then, the precipitates were filtered and washed with distilled water at 40 °C for 2 h and dried at 100 °C for 12 h. Nickel was added by incipient wetness impregnation of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Panreac, Barcelona, Spain). The $Ni(NO_3)_2 \cdot 6H_2O$ amount was calculated in order to obtain a 7 wt% of nickel in the final material. Finally, the impregnated catalyst was dried in an oven at 110 °C during 12 h and afterwards the solids were calcined at 550 °C during 5 h to form the Ni/MgAlO catalyst.

2.2. Catalyst characterization

The support and the nickel catalyst were characterized by physical adsorption of nitrogen at −196 °C in a Micromeritics ASAP 2010 apparatus. XRD analyses were performed using a SIEMENS D-501 diffractometer. Metallic content was established by means of X-ray Fluorescence (XRF) (Broker S4 Explorer). More detailed characterization procedures can be found in previous works [12,13].

2.3. Procedures and analysis

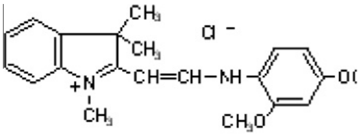
Dye concentration was determined at the wavelength corresponding to the BY11 maximum UV–VIS absorption (Table 1) which was monitored by a Shimadzu UV–VIS spectrophotometer. TOC analyses were performed in a Shimadzu TOC-VCSH appartus, after filtration of the samples (pore diameter 10 mm). The efficiency of catalytic activity, color and TOC removal was evaluated by calculating the ratio between the color and TOC measured at each instant and the values for this parameter for the initial solution. Since TOC analysis only provides information about the global removal of total organic carbon from the liquid-phase, selectivity towards non-organic compounds (S_{NOC}) was defined as 100 (X_{TOC}/X_{dye}) where X_{TOC} and X_{dye} are TOC and dye conversion respectively.

The toxicity of the samples collected at the end of the reaction was measured with a Microtox 500 Analyzer on samples before and after decoloration according to the test protocols defined by the manufacturer (Azur Environmental, Newark, Del.) with a Microtox data analysis program (Microtox Omni Software). This assay is based on the decrease of light emission by *Vibrio fischeri* as the result of its exposure to a toxicant according to ISO 11348-2. The pH of the samples was adjusted to 7.0 ± 0.5. Percentage inhibition of the bioluminescence was obtained mixing 0.5 mL of the final effluent of each experiment and 0.5 mL of the luminescent bacterial suspension. The toxicity of each sample was expressed as the percent of the inhibition of the luminescence relative to a non-contaminated blank (Milli-Q water). Results are given in Toxicity Units (TUs) after 15 min of exposure [12].

2.4. Wet air oxidation and catalytic wet air oxidation experiments

Batch tests were performed in a Hastelloy C22 high-pressure microreactor. The reactor was equipped with an electrically heated jacket and an adjustable speed magnetic stirrer. 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 batch reactor was charged with 100 mL of an aqueous solution of BY11, in the presence of

Table 1
Main characteristics and structure of BY11.

Dye	Structure	Chemical class	C.I. name	C.I. number	Molecular weight (g mol^{-1})	Dye content (%)	Molecular formulae	λ_{max} (nm)
Basic Yellow 11		Cationic dye	Cationic Yellow 11 GI	48055	372.89	20	$C_{21}H_{25}ClN_2O_2$	413