

DECOMPOSITION PATHWAYS AND REACTION INTERMEDIATES FORMATION OF BASIC YELLOW 11 BY NON CATALYTIC AND CATALYTIC WET AIR OXIDATION

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Abstract

In this study, an aqueous solution of Basic Yellow 11 (BY11) was selected as a model to investigate the degradation pathways and to obtain additional information on the reaction intermediate formation. High performance liquid chromatography/mass spectrometry and its tandem mass spectrometry was chosen to identify the decomposition pathways and reaction intermediate formation during the non-catalytic (WAO) and catalytic wet air oxidation (CWAO). The batch oxidation of BY11 has been investigated using a high-pressure reactor at temperatures 130°C and pressures 50 bar. In addition total organic carbon and high performance ion chromatography analysis were employed to obtain further information on the reaction processes during WAO and CWAO. Schematic reaction pathways, which can explain the formation of some byproducts, are proposed.

Introduction

In recent effluents from the dyeing and finishing processes in the textile industry are known to contain high levels of chemicals, high biochemical oxygen demand, total suspended solids and strong color. Azo dyes are generally resistant to degradation by biological treatment methods and as a consequence, their release into the environment poses a serious problem. Textile wastewater contaminated with these azo dyes needs to be treated by physical and chemical means before discharge. In addition to the conventional wastewater treatment methods, advanced oxidation processes (AOPs) are an effective way of degradation for a wide variety of dyes in aqueous solutions.

In this sense, wet-air oxidation (WAO) is an attractive treatment technique for industrial wastewater. Wet air oxidation involves the combustion of pressurized organic matter at relatively high temperatures. Many papers have demonstrated the applicability of WAO to several industrial wastewaters. Most of the compounds studied have a partial order of one with respect to the initial substrate and a variable order with respect to the oxidant. The free-radical mechanism appears to

account for the reactions, and many authors have proposed a number of free-radical reaction pathways without, however, identifying the nature of the radical species formed in the reaction medium. In order to reduce the severity of WAO operating conditions, catalytic wet air processes have been developed (CWAO). The use of catalyst is sought to enhance overall reaction rate and destroy intermediates refractory to noncatalytic oxidation. Milder conditions of temperature and pressure may lower equipment and operation costs. The reaction mechanism of CWAO is thought to be similar to the mechanism of WAO, and the function of the catalyst is essentially that of promoting the formation of free radicals.

Layered Double-metal Hydroxides (LDHs) are one of the nano ordered layered compounds having ability to intercalate anionic compounds, and its has receiving increasing interest in recent years owing to their potential applications in various technologies such as catalysis, adsorption, medicine, electro applications, etc. Therefore, they may be considered promising materials for a large number of possible applications due to their high versatility, easily manipulated properties, wide range of composition and/or preparation variables, low cost, etc.

Non papers have been published on the destruction of Basic Yellow 11 (BY11) by WAO and CWAO. In the present investigation, we have focused our attention on the degradability of the BY11 and the identification of the reaction intermediates formed during the degradation process. The reaction pathways are also discussed.

Methods

Basic Yellow 11 (BY11) was selected as the model pollutant, because it's widely used in the textile, ink, paint, paper, and plastic industries. The azo dye was purchased from Sigma-Aldrich (Steinheim, Germany) and used without further purification. The HT/Ni hydrotalcite-like precursors were synthesized using a wet incipient impregnation of hydrotalcite with metal component. The mass of precursor was calculated in order to obtain 7 wt% nickel in the catalyst. After impregnation, the wet solid was dried overnight at 110°C and then activated under air at 550°C.

The characterization of the support and catalyst were carried out by several techniques as BET, XRD, XRF, TPD/R/O. All the experiments were conducted in a Hastelloy high-pressure microreactor C-276 autoclave Engineers with a volume of 100 mL. The reactor (i.d. 50 mm) was equipped with an electrically heated jacket, a turbine agitator and a variable speed magnetic drive. The reactor was first loaded with 100 mL of solution of commercial dye without or with catalyst (0.4 g), and initially pressurize with nitrogen to ensure inert atmosphere. Afterwards, the system was heated to the desired temperature (130°C) and a sample was withdrawn. Preliminary identifications, which were then verified by HPLC, were also performed with an Agilent 6890N GC/MSD system running in both SCAN and SIM modes of operation.

Results and discussion

When destructive techniques are used, it is interesting to determine the degradation mechanism, the intermediates and the final degradation products.

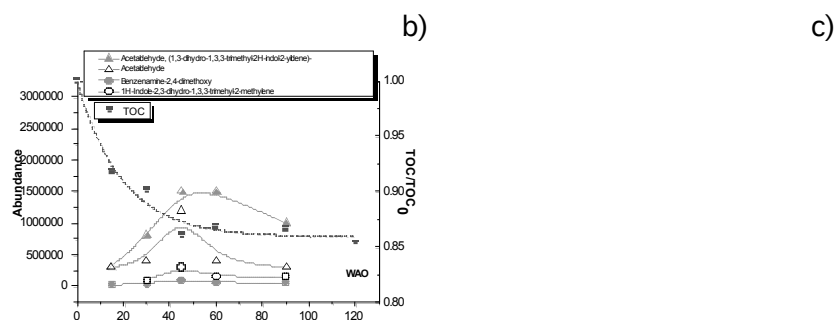


Figure 1. a) Evolution of TOC and reaction intermediates with reaction time in WAO process. b) Evolution of TOC and reaction intermediates with reaction time in CWAO process c) Evolution of dye concentration in WAO and CWAO processes at 130°C, 50 bar, 200 mg.L⁻¹.

The WAO and CWAO processes have been used to degrade Basic Yellow 11. These processes were performed in aqueous acidic medium (pH 5), at 13°C and 50 bar. In Figs 1a,b the concentration profiles of some detected intermediates in WAO and CWAO processes are presented, while Fig. 1 c show a comparison between the dye concentration decay and TOC removal in WAO, CWAO and without catalyst at 130°C. The chromatographic survey by HPLC during the entire processes allowed following the chemical evolution of the solution as a function of reaction time. The dye degradation is more efficient in acidic medium due to the better sensibility of the protonated form for oxidation process. The color loss is visually significant for the reaction time. The electrophilic addition of OH on the azo double bond leads to its rapid breaking. The fast bleaching of the solution and the decrease in the absorption band associated with the –N=N– bond corroborate this suggestion. Detection of degradation products such as hydroquinone confirms this hypothesis. The cleavage of the azo bond is responsible of the chromophoric characteristic loss and generates the formation of aromatic intermediates.

New HPLC peaks indicate the formation of new structures. The production and evolution of BY11 degradation products were followed by liquid chromatography and CG/MS during the WAO and CWAO processes, using a gradient mode to separate compounds formed. The concentration of these intermediates increases to reach a maximum value and then decreases until disappearance. The formation of hydroxylated aromatic derivatives was observed. Some degradation products formed during the CWAO process were identified: (1-3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-

acetaldehyde, 2,4-dimethoxy-bezenamine, 2-methylidoline, acetone, ethanol, 2-hexanoic acid, etc. The identification of degradation products permits us to prove that the first step of azo dye degradation is the azo bond cleavage and the second step is hydroxyl radical addition on the aromatic ring (Garcia et al. 2005).

Conclusions

The degradation of the BY11 by the WAO and CWAO reaction has been studied in aqueous medium. We have shown that both processes are efficient for dye degradation. It is explicitly exhibited by the concentration decrease, color disappearance and TOC decrease in dye solution under study. The degradation mechanism begins with the azo bond cleavage and is followed by the hydroxylation of the aromatic ring. Some degradation products were identified: According to the experimental results, we propose a mechanism reaction pathway for the BY11 mineralization in WAO and CWAO processes.

Acknowledgments

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References

García, J. Gomes, H.T. Serp, Ph. Kalck, Ph. Figueiredo, J.L. and Faria, J.L. (2005). Platinum catalysts supported on MWNT for catalytic wet air oxidation of nitrogen containing compounds. *Catal. Today*, 102-103, 101-109.