ASSESMENT OF HETEROGENEOUS CATALYTIC WET HYDROGEN PEROXIDE OXIDATION ON THE TREATMENT OF INDUSTRIAL WASTEWATERS

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ABSTRACT

Several wastewaters coming from petrochemical, pharmaceutical, agrochemical and printing industries have been treated by application of heterogeneous catalytic wet hydrogen peroxide oxidation (CWHPO). A home-made catalyst based on the immobilization of iron oxide over a mesostructured silica support has been used as heterogeneous catalyst. This catalyst, in pellets form, has shown a remarkable activity under continuous operation in a fixed bed reactor (FBR) working on up-flow mode for all the wastewaters. A high efficiency of the hydrogen peroxide was proven in this process achieving total organic carbon (TOC) removals ranging from 40 to 85 %. Additionally, the deactivation of catalyst was negligible, keeping constant its catalytic performance at steady-state for 55 hours of operation. The increase of other biodegradability parameters, such as the ratio between the biological and chemical oxygen demands (BOD_5/COD) and the average oxidation state (AOS), have also confirmed the efficacy of the CWHPO for the degradation of hazardous pollutants towards more biodegradable by-products.

Keywords: CWHPO, petrochemical, pharmaceutical, agrochemical and printing industries wastewaters

INTRODUCTION

The industrial development and the continuous increasing growth population are responsible of the generation of huge amounts of wastewater with a large number of chemicals and properties non acceptable for the environment and human life. For that reason, the removal of toxic and hazardous compounds from industrial wastewater streams is nowadays a critical task. Chemical pollutants contained in industrial wastewaters are commonly refractory to conventional chemical and biological treatments, and this is often accompanied with biotoxicity behaviour for the microorganisms. Advanced Oxidation Processes (AOPs) are an interesting alternative for the treatment of low biodegradable industrial wastewaters (Sauer et al., 2006; Cañizares et al., 2007). Among AOPs, Fenton´s reagent has emerged as an interesting alternative for the treatment of dissolved organic pollutants in wastewater streams (Fenton, 1984). Besides basic studies using model pollutants and synthetic wastewaters prepared in laboratory, Fenton-like reactions have been efficiently used as oxidation processes for the treatment of real industrial wastewaters (Pérez et al., 2002; Kurt et al., 2006; Bautista et al., 2008). In all cases, usual drawbacks associated to this technology are the limited range of the pH (2-3) in which the reaction proceeds and the need for recovery of homogeneous catalyst to comply with the environmental regulations. In order to avoid the problems coming from the homogeneous Fenton catalysts, our research group has designed a solid catalyst consisting of a crystalline Fe_2O_3/SBA-15 nanocomposite, which exhibits a high degradation rate for the mineralization of phenolic aqueous solutions and industrial wastewaters in a wide range of pH, using moderate amounts of oxidant and with a remarkable stability of the iron oxides on the silica support (Melero et al., 2007). This material has been extruded in pellets and used in catalytic fixed bed reactors (Martínez et al., 2007). This work summarizes the results of the treatment of four wastewater streams coming from different industries (petrochemical, pharmaceutical, agrochemical and printing factories) by heterogeneous catalytic wet hydrogen peroxide oxidation in a fixed bed reactor.

METHODS

Industrial wastewaters: Origin and Characterization

Four wastewater streams produced in different industries were treated by means of the CWHPO system. The effluent coming from the pharmaceutical industry is a mixture of different organic compounds, such as oxygenated solvents and alcohols. The petrochemical wastewater was produced in a styrene factory and contained majorly aromatic and other organic compounds. Printing factory wastewater is a mixture of compounds cleaning water process and spent developer containing solutions. Finally, wastewater coming from an agrochemical industry is mainly characterized by the presence of different fungicides and herbicides. The physicochemical characterization of the wastewaters streams is shown in Table 1.

Table 1. Physicochemical characterization of the industrial wastewaters

	Pharmaceutical Wastewater	Petrochemical Wastewater	Printing Factory Wastewater	Agrochemical Wastewater
TOC (g/L)	1.7	44	9	8
COD (g/L)	3.8	139	33	28
BOD_5 (g/L)	0.76	17.7	0.04	N.A.
pH	5.6	12.2	4.5	5.6
Cl^- (g/L)	6.77	< Q.L.	0.02	N.A.
$[NO_3^-]$ (g/L)	1.00	14.8	0.16	0.01
$[NH_4^+]$ (g/L)	0.01	< Q.L.	< Q.L.	0.21
$[CO_3^{2-}]$ (g/L)	< Q.L.	23.1	N.A.	< Q.L.
$[HCO_3^-]$ (g/L)	0.22	< Q.L.	N.A.	< Q.L.

Q.L. Quantification limit; N.A. Non-available data.

Catalyst Preparation and Characterization

Iron oxide supported into a SBA-15 mesostructured material was prepared by a co-condensation of silica (TEOS) and iron ($FeCl_3 \cdot 6H_2O$) sources templated by pluronic 123 as described elsewhere (Melero et al., 2007). After that, the powder material was extruded with sodium bentonite and synthetic methylcellulose polymer for the preparation of cylindrical pellets with ca. 2 mm of internal diameter and 2 mm of height, for its application in a fixed bed reactor (Martinez et al., 2007). The Fe_2O_3/SBA-15 pellets can be described as a composite material that contains different iron oxides particles (mainly crystalline hematite) embedded on a mesostructured SBA-15 matrix. The total iron content was around 14 % wt., and the support exhibits a BET surface area of ca. 265 m^2/g.

Catalytic Wet Hydrogen Peroxide Oxidation experiments

The continuous CWHPO experiments were carried out in an up-flow fixed bed reactor (FBR) with 1.2 cm of inner diameter and 15 cm of length, working under atmospheric pressure. The catalytic packed bed was formed by 2.9 g of pellets. An appropriate mixture of wastewater and hydrogen peroxide, acidified up to pH 3 has been used as inlet stream and pumped to the packed bed reactor by means of a Gilson 10SC HPLC pump operating at 0.25 mL/min. The temperature of the reactor was controlled at 80 °C on the upper part of catalytic packed bed reactor. Total Organic Carbon (TOC), hydrogen peroxide and iron concentrations in the outlet stream after treatment were monitored with the time on stream in order to determinate the efficiency of the oxidation process and the stability of the heterogeneous iron catalyst. Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD_5) were measured at final steady-state conditions to complete the characterization of the treated effluent.

RESULTS AND DISCUSSION

Several variables were studied for the treatment of the four wastewaters, such as the potential application of CWHPO for the treatment of wastewater as-received and diluted samples, and the influence of hydrogen peroxide amount. In the results reported herein (Table 2), the four wastewaters were treated under comparative operation conditions, in order to evaluate the influence of the wastewater in nature. Thus, the wastewaters samples were diluted until initial TOC concentrations ranging from 800 to 1100 mg/L and the initial hydrogen peroxide concentration was set to twice the stoichometric amount for the theoretical total TOC mineralization. The petrochemical wastewater resulted in the most stable one with just 40 % of TOC reduction. In the case of the other wastewaters, remarkable TOC conversions between 60 and 85 % were obtained. Likewise, the BOD_5/COD ratio and the average oxidation state (AOS) of the outlet effluent after treatment always increased. This fact was particularly relevant for the printing wastewater, with characteristic BOD_5/COD values of conventional urban wastewaters. In terms of the catalyst stability and deactivation phenomena, the amount of iron detected in the outlet effluent was always lower than 1 mg/L and the catalytic performance in terms of TOC conversions was kept constant up to 55 hours of operation.

Table 2. Wastewater characterization of the inlet and treated effluent by the CWHPO system

	Pharmaceutical Wastewater		Petrochemical Wastewater		Printing Factory wastewater		Agrochemical Wastewater	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
TOC (g/L)	0.86	0.35	1.1	0.65	0.9	0.12	0.8	0.21
COD (g/L)	1.9	0.36	3.47	0.86	3.3	0.17	2.8	1.38
BOD_5 (g/L)	0.38	0.11	0.44	0.16	0.004	0.086	N.A.	N.A.
BOD_5/COD	0.2	0.3	0.13	0.19	0.001	0.5	N.A.	N.A.
AOS	0.7	2.47	-0.73	2.02	-1.5	1.85	-0.44	0.85
H_2O_2 (g/L)	12.04	0.66	15.4	< Q.L.	12.6	0.02	11.2	2.57
Fe (mg/L)	-	< Q.L.	-	0.7	-	< Q.L.	-	0.27
X_{TOC} (%)	-	59.3	-	40.9	-	86.7	-	73.7
X_{H2O2} (%)	-	94.5	-	100	-	99.8	-	77

Q.L. Quantification limit; N.A. Non-available data.

CONCLUSIONS

The CWHPO studied in this work, based on a continuous fixed bed reactor employing pellets of Fe_2O_3/SBA-15, has provided a remarkable TOC mineralization and an increase of biodegradability for the different industrial wastewaters. These results prove the potential application of heterogeneous CWHPO with a moderate use of hydrogen peroxide to reduce the organic loading of the industrial wastewaters and/or make them more biodegradable in case of subsequent biological processes.

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