

INTEGRATED HETEROGENEOUS CATALYTIC WET HYDROGEN PEROXIDE OXIDATION AND AEROBIC BIOLOGICAL TREATMENT OF AN INDUSTRIAL AGROCHEMICAL WASTEWATER

J.A. Siles¹, I. Pariente², R. Molina², F. Martínez², J.A. Melero²

¹Department of Inorganic Chemistry and Chemical Engineering, University of Cordoba, Campus Universitario de Rabanales, Edificio Marie Curie, Ctra. N-IV, km 396, 14071, Cordoba, Spain. Email: a92siloj@uco.es ²Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, 28933, Mostoles, Madrid, Spain. Email: isabel.pariante@urjc.es; raul.molina@urjc.es; fernando.castillejo@urjc.es; juan.melero@urjc.es

Abstract

The aim of this study was to evaluate at lab-scale the viability of an integrated chemical-biological oxidation process to treat highly polluted wastewater from an agrochemical plant. The first step was a continuous and heterogeneous catalytic wet hydrogen peroxide oxidation system (CWHPO) followed by an aerobic biological post-treatment using rotating biological contactors (RBC). The oxidation system consisted of a fixed bed reactor, employing hydrogen peroxide as oxidant and pellets of Fe₂O₃/SBA-15 as heterogeneous catalyst. After the CWHPO step, a marked reduction in the total organic carbon (TOC) content of the wastewater (ca. 50% under steady-state conditions) and total hydrogen peroxide consumption was observed in the outlet effluent, which favours the possibility of a subsequent coupling with a conventional biological treatment. The effluent of the CWHPO was mixed with a synthetic municipal wastewater solution at a proportion of 1%, 5% and 10% (v/v) and its aerobic co-treatment was evaluated. The results showed that the mixture was highly biodegradable achieving TOC reduction of 78% for the highest load. Additionally, a marked decrease in total nitrogen concentration (50%) was observed in the effluent of the biological treatment, which indicates that the proposed treatment is a good alternative for treating wastewater from agrochemical industry.

Keywords: Agrochemical wastewater, CWHPO, aerobic treatment, RBC.

Introduction

Recently, a rather fast evolution of the research activities devoted to environment protection has been recorded as a consequence of the delivery of very severe regulations. The fulfilment of quality standards is especially claimed for those substances exhorting toxic effects on the biological sphere preventing the activation of biological degradation processes (Andreozzi *et al*, 1999). Pesticides are among the major organic compounds encountered as pollutants in wastewater effluents of agrochemical industries. These compounds are toxic and carcinogenic in nature even at low concentration. Consequently, many treatment processes have been applied for their removal from industrial wastewater, including advanced oxidation processes (AOPs) (Lafi & Al-Qodah, 2006). AOPs involve the generation of non-selective and highly reactive hydroxyl radical (HO·), which is one of the most powerful oxidation agents (Glaze *et al*, 1987). Among them, Fenton's reagent has emerged as an interesting alternative for the treatment of dissolved organic pollutants in wastewater streams

(Fenton, 1984). In some cases, temperature has been increased up to 80–120°C leading to the so-called CWHPO processes, which can be used as a pre-treatment step for converting inhibitory compounds to more readily biodegradable intermediates or to the point where the inhibition effect of these compounds on a biological treatment is not significant. However, very little information has been cited in the literature regarding the applications of combined AOPs with biological treatment to eliminate toxic chemicals found in wastewater streams from agrochemical industries. The aim of this study was to evaluate the treatment of wastewater from an agrochemical plant, which manufactures pesticides, by a CWHPO system combined with a biological post-treatment using a RBC at laboratory scale.

Methods

Wastewater: Nature and characterization

The wastewater used as substrate in this study derived from an agrochemical manufacturing industrial plant focussed on the synthesis of different insecticides, herbicides and fungicides. The physicochemical characterization of the wastewater sample is depicted in Table 1.

Table 1. Physicochemical characterization of the agrochemical wastewater.

Parameter	Value	Parameter	Value
pH	5.65	TKN (mg/L)	1085
λ (mS/cm)	3.76	NO_3^- (mg/L)	10.1
Turbidity (NTU)	9320	NO_2^- (mg/L)	< Q.L.
COD (mg O_2 /L)	28000	NH_4^+ (mg/L)	209
TOC (mg/L)	9450	SO_4^{2-} (mg/L)	< Q.L.
CO_3^{2-} (mg/L)	< Q.L.	Suspended solids (g/L)	8.4
HCO_3^- (mg/L)	< Q.L.	AOS	-0.44

Conductivity; TKN: Total Kjeldahl Nitrogen; AOS: Average Oxidation State; Q.L.: Quantification limit.

Catalyst Preparation and Characterization

$\text{Fe}_2\text{O}_3/\text{SBA-15}$ catalyst was synthesized by direct co-condensation of silica (TEOS) and iron ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) sources in presence of Pluronic 123 molecules following the method described elsewhere (Melero *et al*, 2007). $\text{Fe}_2\text{O}_3/\text{SBA-15}$ extrudates were prepared by blending of the powder catalyst with sodium bentonite (75:25 wt %) and synthetic methylcellulose polymer (10 wt. % of the previous mixture) which act as binders in the extrusion process (Martínez *et al*, 2007). The total iron content was around 14% wt., and the support exhibits a BET surface area of ca. 265 m^2/g .

Experimental set-up

The experimental set-up used for the CWHPO experiments consisted of an up-flow fixed bed reactor working under continuous conditions and atmospheric pressure. It was made of glass with 1.2 cm of inner diameter and 15 cm of length. The catalyst particles were packed between glassy beads to enable better distribution of the inlet wastewater inside the catalyst bed. The operation conditions

were set according to preliminary studies (Martínez *et al*, 2007; Melero *et al*, 2009): 0.23 g_{H₂O₂}/g_{TOC}, 80°C, 11.6 g·min/mL of residence time and wastewater pH of 3. Under these conditions wastewater was continuously pumped to the packed bed reactor by means of a Gilson 10SC HPLC pump. On the other hand, a 21-L Rotating Biological Contactor (RBC) from ACAI Depuracion S.L. was used for the biological post-treatment of the oxidised wastewater. The system was made of thick stainless steel sheet AISI 304 and consisted of four stages, which were separated by fixed baffle plates with 5 discs in each compartment. The diameter of each disc was 30 cm and the total surface area for biomass attachment was 2.83 m². Around 40% of disks are submerged in water. The reactor was inoculated with aerobic sludge from an urban wastewater treatment plant and fed with a synthetic solution which simulates the features of the inlet stream in a biological wastewater treatment plant (Kositzki *et al*, 2004).

CWHPO and biological integration

The effluent from the CWHPO was characterised and mixed with the synthetic solution at proportions of 1%, 5% and 10% (v/v). Each assay lasted between 21 and 28 days; the time interval required to reach the steady-state conditions. The following parameters were determined in the industrial wastewater, synthetic solution and in the effluents of the CWHPO and RBC during the experimentation time: pH, chemical oxygen demand (COD), TOC, NO₃⁻, NO₂⁻, NH₄⁺ and SO₄²⁻. Each analyse was carried out at least in duplicate in accordance with the Standard Methods (APHA, 1998) and the results expressed as average of the duplicate measurements.

Results and discussion

TOC conversion in the CWHPO remained virtually stable across the experiments, reaching a mean value of ca. 50% under steady-state conditions. By increasing the mixing percentage of oxidized and synthetic wastewater from 1% to 5% and 10%, TOC conversion in the RBC slightly varied, reaching the highest value (78%) for the mixing percentage of 10%. This fact indicates that biomass was able to adapt to increasing concentrations of oxidized wastewater in the RBC influent. Figure 1 shows the TOC concentrations in the RBC inlet and outlet effluents at mixing percentage of 5% and 10%. On the other hand, a strong reduction in total nitrogen concentration (50%) was observed after the biological step.

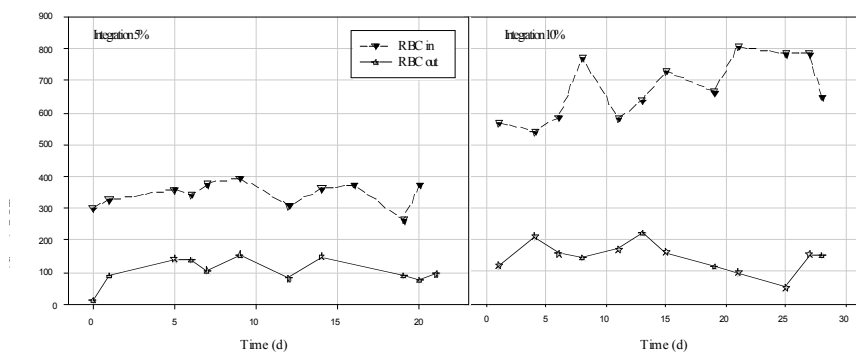


Figure 1. Variation of TOC in the RBC inlet and outlet effluents at integration percentages of 5 and 10%.

Conclusions

The results obtained in this study indicate that the integration of CWHPO and RBC is a good alternative for treating wastewater from agrochemical industry. The CWHPO system based on a continuous fixed bed reactor employing pellets of $\text{Fe}_2\text{O}_3/\text{SBA-15}$ in a catalytic packed bed, removed a high percentage of TOC and increased the biodegradability of the remnant organic matter. The biological post-treatment allowed a marked reduction of TOC and total nitrogen in the effluent of the oxidation step, which strongly reduces the environmental toxic effect of the studied wastewater. Additionally, the biomass in the RBC is highly adaptable to increasing concentrations of the effluent from the CWHPO reactor, opening out the range of operation conditions for the integrated system.

References

- Andreozzi, R., Caprio, V., Insola, A. and Marotta, R. (1999). Advanced oxidation processes (AOP) for water purification and recovery. *Catal. Today*, 53, 51–59.
- Standard Methods for the Examination of Water and Wastewater (1998). 20th edn, American Public Health Association (APHA), Washington DC, USA.
- Fenton, H. J. (1984). Oxidation of tartaric acid in presence of iron. *J. Chem. Soc.*, 65, 899–910.
- Glaze, W.H., Kang, J.W. and Chapin, D.H. (1987). The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Sci. & Technol.*, 9, 335–352.
- Kositzi, M., Poullos, I., Malato, S., Cáceres, J. and Campos, A. (2004). Solar photocatalytic treatment of synthetic municipal wastewater. *Water Res.*, 38, 1147–1154.
- Lafi, W.K. and Al-Qodah, Z. (2006). Combined advanced oxidation and biological treatment processes for the removal of pesticides from aqueous solutions. *J. Hazard. Mater.*, B137, 489–497.
- Martinez, F., Melero, J.A., Botas, J.A., Pariente, M.I. and Molina, R. (2007). Treatment of phenolic effluents by catalytic wet hydrogen peroxide oxidation over $\text{Fe}_2\text{O}_3/\text{SBA-15}$ extruded catalyst in a fixed bed reactor. *Ind. Eng. Chem. Res.*, 46, 4396–4405.
- Melero, J.A., Calleja, G., Martínez, F., Molina, R. and Pariente, M. I. (2009). Nanocomposite $\text{Fe}_2\text{O}_3/\text{SBA-15}$: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions. *Chem. Eng. J.*, 131, 245–256.