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# Treatment of an agrochemical wastewater by integration of heterogeneous catalytic wet hydrogen peroxide oxidation and rotating biological contactors

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## HIGHLIGHTS

- Agrochemical wastewater treatment by catalytic peroxide oxidation and biological system.
- Oxidation reduced significantly the total organic carbon and increased its biodegradability.
- Remarkable performance and stability of the rotating biological contactors.
- Treated effluent fulfilled the mandatory values of the regional law.

## ARTICLE INFO

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## ABSTRACT

The treatment of a non-biodegradable agrochemical wastewater has been studied by coupling of heterogeneous catalytic wet hydrogen peroxide oxidation (CWHPO) and rotating biological contactors (RBCs). The influence of the hydrogen peroxide dosage and the organic content of the wastewater (dilution degree) were studied. The CWHPO of the raw wastewater at 80 °C and using a moderate amount of oxidant (0.23 $gH_2O_2/gTOC$) reduced significantly its total organic carbon content and increased its biodegradability. Likewise, the iron leaching of the heterogeneous catalyst ($Fe_2O_3$/SBA-15) was less than 2 mg/L in the treated effluent. Under the best operating conditions, the resultant CWHPO effluent was successfully co-treated by rotating biological contactors (RBCs) using a simulated municipal wastewater with different percentages of the CWHPO effluent (2.5, 5 and 10% v/v). The RBCs showed high stability for the treatment of the highest percentage of the CWHPO effluent, achieving total organic carbon (TOC) and total nitrogen (TN) reductions of ca. 78% and 50%, respectively. The integration of both processes on a continuous mode has been successfully accomplished for the treatment of the as-received agrochemical wastewater.

## 1. Introduction

There is a large scale development of pesticides during the last few decades due to its fundamental role in food and fibre productions. In recent years, the presence of pesticides in water and food [1] and their adverse effects on the human health and the equilibrium of the ecosystems [2] have paid the attention of different investigations [3]. The monitoring of these compounds over the last 20 years have highlighted some chronic effects such as carcinogenesis [4], neurotoxicity [5], sterility [6] and cell development effects, particularly in the early stages of life [7]. These substances are present in wastewaters coming from agrochemical plants dedicated to the manufacture of pesticides and industries of food manufacturing. Their critical effect on the environment and human health makes necessary the degradation of these compounds by efficient and friendly-environmental technologies [3].

Biological processes are the most attractive treatments in terms of economic costs and environmental concerns. However, they do not always provide satisfactory results, especially for the treatment of industrial wastewaters, since many of the containing organic substances are toxic or resistant to biological degradation [8,9]. In this sense, other kind of technologies such as advanced oxidation processes (AOPs) has emerged as promising alternatives for the treatment of industrial wastewaters with highly refractory and toxic pollutants [10,11]. These processes are based on the

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generation of non-selective and highly reactive hydroxyl radicals ($HO^{\cdot}$), which are ones of the most powerful oxidation agents [12].

Among the AOPs, several works have been published for the treatment of wastewaters containing pesticides, using UV radiation alone or in presence of hydrogen peroxide [13] or $TiO_2$ as heterogeneous photocatalysis [14]. In other cases, ozonation or ultrasonic-based processes have been also used [15]. In all the cases, the efficiency of these technologies was significant limited to low pollutant concentrations.

Other AOP that is often employed for the treatment of more concentrated effluents is Fenton technology [16]. The oxidation of different pesticides by means of Fenton-like reactions using ferrous salts and hydrogen peroxide has been studied in numerous works during last years [17]. Nowadays, Fenton technology is commercially used to treat different kind of industrial wastewaters [18]. To overcome typical limitations of homogeneous Fenton catalytic systems, strong pH dependence ranging ca. from 2.5 to 3.5 and recovery of dissolved iron species as sludge in a final separation step, several types of heterogeneous Fenton-like catalysts have been developed in the last decades [19–23]. In particular, our research group has synthesized a catalyst based on supporting crystalline iron oxides over a mesoporous SBA-15 silica matrix [20]. This catalyst has been successfully used for the degradation of phenol as model pollutant [24,25] and an industrial wastewater [10], using temperatures between 80 and 120 °C as so-called catalytic wet hydrogen peroxide oxidation (CWHPO) process.

The operating conditions of CWHPO systems are normally focused on the mineralization of the organic loading [26]. In this sense, the economical feasibility of CWHPO is often questioned by the high oxidant consumption and the energetic costs of the operation temperature. However, from other point of view, CWHPO can be also used at milder operation temperatures and moderate oxidant dosages, as pretreatment obtain a more biodegradable effluent for a subsequent biological process instead of increasing the TOC mineralization [27].

For the coupling of CWHPO and biological processes, the application of heterogeneous catalysts in CWHPO is also a crucial point. As compared to homogeneous systems, the heterogeneous catalysts prevent additional metal pollution and therefore, costly separation units for its recovery, making simpler the integration of both processes. As far as we know, few works are described in literature coupling heterogeneous CWHPO processes and biological systems [28,29].

In the studies of coupling processes, the biological treatment is normally based on suspended growth batch reactors as activated sludge-like processes [30]. However, limited work has been carried out using attached growth reactors such as rotating biological contactors (RBCs). Recently, several works have shown the potential of RBCs for the treatment of different complex wastewaters, due to the large active surface and high biomass concentration, which allow high organic loading rates and short hydraulic retention times (HRT) with a robust stability of the process [31,32]. In this sense, a palm oil mill effluent (POME) was treated in an activated sludge system using a diluted raw wastewater (5000 mg/L of COD concentration) with a HRT of 36 h, obtaining a COD removal efficiency of 42% [33]. In contrast, RBCs were able to treat a concentrated POME (ca. 23500 mg/L of COD concentration) obtaining a COD removal efficiency higher than 70% for the same HRT [34].

In this work, the treatment of a non-biodegradable wastewater from an agrochemical plant has been studied by coupling of heterogeneous catalytic wet hydrogen peroxide oxidation (CWHPO) and rotating biological contactors (RBCs) as biological treatment. The heterogeneous CWHPO system has been evaluated in terms of increasing the biodegradability of the agrochemical wastewater for feasible co-treatment of the CWHPO effluent with a simulated municipal wastewater in the subsequent RBCs. Up to date, this fully integration of heterogeneous CWHPO with a biological treatment is considered one the first approaches to the treatment of real wastewaters with a high stability of both heterogeneous catalyst of advanced oxidation process and biological treatment.

## 2. Materials and methods

### 2.1. Agrochemical wastewater characterization

The studied wastewater was taken from an agrochemical manufacturing industrial plant located in Madrid (Spain), which is dedicated to the synthesis of different kind of pesticides. The characterization data of the as-received wastewater is shown in Table 1.

### 2.2. CWHPO experimental set-up

The CWHPO system consists of a fixed bed reactor made of glass with an inner diameter of 1.2 cm and 15 cm of length. As catalyst, crystalline iron oxides supported over a mesoporous SBA-15 silica matrix was used. The catalyst was conformed as extrudates of 2.0 mm × 1.5 mm following a methodology described elsewhere [25]. The pellets show crystalline hematite entities of ca. 14 wt.% of iron content and the main properties of SBA-15 topology, such as mesoscopic order and narrow pore diameter distribution, with a BET surface of about 264 $m^2/g$. The catalyst particles are packed between glassy beads to enable a better distribution of the inlet solution inside the catalytic bed. A schematic view of the CWHPO experimental set-up is shown in Fig. 1a.

The wastewater feed was acidified until a pH value of ca. 3 by addition of a sulphuric acid solution 1 M. After addition of appropriate amount of hydrogen peroxide, it was pumped by a Gilson 10SC HPLC pump to the reactor. The temperature of the reactor was controlled by the circulation of a heating fluid (silicone) along an external jacket. The residence time and temperature were kept constant according to preliminary studies using the same experimental set-up at 11.6 min and 80 °C, respectively [10,25]. The residence time was calculated according to Eq. (1), being $w_{CAT}$ the catalyst weight and $Q_F$ and $\rho_F$ the volumetric flow and the density of the feeding stream, respectively. Samples from the treated effluent were withdrawn across the experiments in order to monitor the performance of the CWHPO runs. Prior to coupling experiments, the feasibility of treating the as-received wastewater without dilution and the optimal hydrogen peroxide were studied.

$$\tau = \frac{w_{CAT}}{Q_F \cdot \rho_F} \tag{1}$$

**Table 1**
Agrochemical wastewater characterization before and after the CWHPO treatment. Operation conditions: $T = 80$ °C, $\tau = 11.6$ min, $pH_0 = 3$, $[H_2O_2]_0 = 0.23\ gH_2O_2/gTOC$.

| Parameter | Industrial wastewater[a] | Oxidized wastewater[a] | Limit value[b] |
|---|---|---|---|
| COD (mg $O_2$/L) | 28067 ± 722 | 13693 ± 431 | 1750 |
| TOC (mg/L) | 9040 ± 440 | 4539 ± 609 | – |
| $BOD_5$ (mg $O_2$/L) | 2100 ± 205 | 1860 ± 82 | 1000 |
| $BOD_5$/COD | 0.07 | 0.13 | – |
| pH | 5.7 ± 0.1 | 3.2 ± 0.1 | 6–10 |
| $NO_3^-$ (mg/L) | 13 ± 4 | 11 ± 8 | – |
| $NO_2^-$ (mg/L) | <0.01 | <0.01 | – |
| $N_T$ (mg/L) | 688 ± 57 | 605 ± 50 | 125 |

[a] Number of samples analyzed = 3.
[b] Emission limit value according to Comunidad de Madrid Legislation.