TREATMENT OF AN AGROCHEMICAL WASTEWATER BY INTEGRATION OF HETEROGENEOUS CATALYTIC WET HYDROGEN PEROXIDE OXIDATION AND ROTATING BIOLOGICAL CONTACTORS

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Published on:


doi: http://dx.doi.org/10.1016/j.cej.2013.04.081
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 gH₂O₂/gTOC) reduced significantly its total organic carbon content and increased its biodegradability. Likewise, the iron leaching of the heterogeneous catalyst (Fe₂O₃/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.

Keywords: Pesticides; Agrochemical wastewater; Catalytic wet hydrogen peroxide oxidation; Rotating biological contactors; Biodegradability.
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 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 significantly 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 ºC 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. CWHP experimental set-up

The CWHP 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 x 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 CWHP experimental set-up is shown in Figure 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 equation 1, being $w_{\text{CAT}}$ 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.

$$\tau = \frac{w_{\text{CAT}}}{Q_F \cdot \rho_F}$$  
Eq.1.

2.3. Rotating Biological Contactor system (RBC)

The rotating biological contactors (RBC) at lab-scale were used for the biological treatment of the previously oxidized wastewater. The bioreactor is made of AISI 304 stainless steel and has a total volume of 5.25 L with five discs. The diameter of each disc is 30 cm and the total surface area for biomass attachment is 0.71 m², being around 40% of each disc submerged in water. The disc rotational speed was 30 rpm. During the preliminary starting-up step and prior to the combination with the CWHPO effluent, the organic loading rate was 2 g$_{\text{TOC}}$/day·m². A schematic representation of the RBC experimental setup is shown in Figure 1b. The RBCs were inoculated with biomass coming from an urban wastewater treatment plant located at Rey Juan Carlos University (Spain) of ca. 2600 inhabitants equivalent, which is operated by RBCs as secondary treatment with 17 g$_{\text{COD}}$/day·m² of organic loading rate, and ca. 200 mg/L and 60 mg/L of COD in the inlet and outlet effluents, respectively. Thereafter, the RBCs were fed batch-wise for 25 days [35] with a synthetic municipal wastewater [36] that contains peptone (160 mg/L), meat extract (110 mg/L), urea (30 mg/L), $K_2\text{HPO}_4$ (28 mg/L),
NaCl (7 mg/L), CaCl₂ (4 mg/L) and Mg₂SO₄ (2 mg/L) and sucrose (100 mg/L) as additional carbon source until the formation of an homogeneous biofilm attached to the RBCs. After that period of time, the RBCs were continuously fed with the same simulated wastewater previously indicated but without sucrose for 66 days.

2.4. CWHPO and biological integration

Once the RBCs were stabilized and acclimatized, the integration of the CWHPO with the RBCs was carried out. In the integrated system, the effluent of the CWHPO was fed with the synthetic municipal wastewater at different volumetric ratios (2.5, 5 and 10 %) and constant feed flow rate of 10 mL/min. As the process was fully coupled and the hydraulic retention time of RBCs was maintained constant (8.75 hours), a higher production of the CWHPO effluent was needed when the volumetric ratio was increased. In order to provide a higher volumetric flow of the treated CWHPO effluent, the CWHPO feed flow rate was increased, but also with the catalyst mass (0.25, 0.5 and 1 mL/min with 2.9, 5.8 and 11.6 g, respectively). Thus, the residence time of the catalytic fixed bed reactor, as defined in Equation 1, was maintained constant for the three volumetric ratios (2.5, 5 and 10%).

An overall schematic representation of the integrated experimental set-up of the CWHPO and the RBCs for the treatment of the agrochemical wastewater is shown in Figure 1. The performance of the integrated system was evaluated by analysis of the samples taken from the simulated municipal (1) and industrial wastewater (2) tanks, the CWHPO effluent (3), the RBC feed (4) and treated effluent (5).
2.5. Analytical methods

Total organic carbon (TOC) content of the solutions was analysed using a combustion/non dispersive infrared gas analyser model TOC-V Shimadzu, which was calibrated with a standard solution of potassium phthalate prior to the TOC analyses. Metamitron, one of the herbicides detected in the composition of the wastewater, was analyzed using a HPLC chromatograph (Varian Prostar) equipped with a Waters dC18 column and an UV detector. Measurements of UV–Vis absorption carried out at 220 nm in a Varian Cary 500 Scan UV–VIS–NIR spectrophotometer were also used as indirect indicator of pollutants with chromophore groups such as aromatic rings, which are characteristic of herbicide compounds. For the treated solutions of the CWHPO runs, the conversion of the hydrogen peroxide was determined by iodometric titration and the iron content was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis collected in a Varian VISTA AX system. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were determined following the procedures described by APHA [37]. On the other hand, NO$_3^-$, NO$_2^-$, total nitrogen (TN) and SO$_4^{2-}$ were measured by colorimetric methods (Maxidirect, Lovibond) at different wavelengths [37].

Aerobic biodegradability of the as-received wastewater and samples after CWHPO treatment were assessed by Zahn-Wellens bioassays [38]. Typically, 0.2 L of sample with a COD concentration of ca. 1000 mg/L is firstly neutralized with NaOH up to a pH of 7.0. Thereafter, 4 mL of sludge with ca. 2 g/L of suspended solids coming from the urban wastewater treatment plant located at Rey Juan Carlos University, was added to the previous solution and shaken at 150 rpm under diffuse illumination at room temperature. The biodegradability of samples was estimated from the COD removal for
3. Results and discussion

3.1. Evaluation of catalytic wet hydrogen peroxide oxidation process (CWHPO)

The as-received agrochemical wastewater showed a low biodegradability according to the BOD$_5$/COD ratio (0.07) with a relatively high TOC concentration (9.4 g/L) (see Table 1). These characterization data make necessary the CWHPO treatment prior to the biological treatment. In many studies, the dilution of the original wastewaters has been used in order to achieve a good catalytic performance. In this study, the efficiency of the CWHPO was evaluated for the as-received wastewater at different dilution degrees. Likewise, the dosage of hydrogen peroxide is a crucial issue in CWHPO processes, particularly from the economic point of view due to its high consumption. In the case of using CWHPO as pretreatment for a subsequent biological process, the influence of the hydrogen peroxide concentration was studied in order to maximize its efficiency in the production of a biodegradable effluent and to minimize the amount of oxidant unconverted after reaction.

Thus, preliminary experiments were carried out with inlet streams of TOC contents ranging from wastewater samples ten times diluted (0.9 g/L) up to the as-received wastewater without dilution (9.4 g/L). Temperature, oxidant dosage and residence time were kept constant at 80 °C, 3.5 gH$_2$O$_2$/gTOC and 11.6 min, respectively. As seen in Figure 2, a constant TOC conversion was achieved regardless of the inlet organic content. However, the hydrogen peroxide conversion reached values of 60 % for the most diluted inlet stream, decreasing until 26 % for the as-received wastewater. Taking into account that the initial oxidant/TOC ratio was constant for all the experiments (3.5...
gH$_2$O$_2$/gTOC), the decrease of the hydrogen peroxide conversion could be attributed to the catalyst deactivation by strong adsorption of organic compounds when higher TOC concentrations are used. On the other hand, the similar TOC conversions, even though with different oxidant consumptions, seem to indicate the mineralization of the organic matter by thermal degradation in some extension. This fact was confirmed by a blank experiment at the same temperature but in absence of catalyst and hydrogen peroxide. In terms of the TOC conversion, the performance of the blank experiment was slightly lower than the CWHPO one. However, the CWHPO experiment revealed a remarkable degradation of metamitron (85 %), one of the major toxic pollutants detected in this wastewater, as compared to the blank experiment with negligible degradation.

The influence of the inlet TOC concentration on the iron leaching of the heterogeneous catalyst in the liquid phase was also evaluated (Figure 2). As can be seen, the iron concentration of the outlet effluent for as-received wastewater was ca. 17 mg/L. In turn, a significant decreasing was gradually observed as the wastewater was diluted. This is in agreement with the hypothesis that organic substrate plays an important role on the catalyst leaching. Therefore, aromatic compounds seem to be responsible of reductive-oxidative reactions over the iron sites of the catalyst that promotes its dissolution in the liquid phase [25]. Other studies in literature have postulated that some by-products could form complexes with the supported iron [39], being responsible of the iron leaching.

In order to make the CWHPO economically attractive, the use of small oxidant dosages is recommended. Additionally, when a subsequent biological treatment is considered after CWHPO, the amount of oxidant should be limited to degradation of toxic and/or non-biodegradable pollutants to oxidized by-products amenable to biological treatment.
At the same time, the amount of unconverted oxidant must be reduced in order to preserve the microorganism population. In this study, several experiments were carried out varying the hydrogen peroxide concentration in the as-received wastewater feed stream from 3.5 to 0 gH₂O₂/gTOC, whereas residence time (11.6 min), temperature (80 °C) and acidification of the wastewater were kept constant. Figure 3 shows the results of these experiments according to different variables: the removal of TOC, the hydrogen peroxide conversion, UV-VIS absorbance at 220 nm, and the iron concentration in the outlet effluent for the different hydrogen peroxide/TOC ratios.

The influence of the hydrogen peroxide was not very significant in terms of TOC mineralization, achieving values of ca. 55% even in the absence of the oxidant. However, some interesting results were obtained taking into account other characterization data related to the composition of the residual organic content. Thus, it was seen that a minimum hydrogen peroxide dosage (0.23 gH₂O₂/gTOC) yielded a significant reduction of the UV-VIS absorbance (characteristic of pesticide pollutants containing aromatic compounds) and metamitron. The increase of the oxidant concentration only showed a beneficial reduction of metamitron from 34 to 85%.

Concerning the catalyst stability, the lowest amount of iron leaching was attested for the smallest oxidant dosage, with iron concentrations below 2 mg/L, which is a crucial point not only for the life of catalyst but also for the subsequent integration with the biological treatment. Regarding the oxidant conversion, the maximum conversion (nearly 95%) was achieved using the lowest oxidant dosage.

According to these results, 0.23 gH₂O₂/gTOC was considered the optimum oxidant dosage for CWHPO of the agrochemical wastewater as pre-treatment prior to final biological treatment. For this oxidant dosage, further characterization such as the BOD₅
and COD, the conductivity, the turbidity and the nitrogen content in different forms were assessed. Table 1 shows the characterization data of as-received wastewater and the CWHPO effluent (permitted values of some parameters according to the current legislation were also included). Biodegradability profiles of both samples for Zahn-Wellens bioassays were also evaluated (Figure 4). From all these results, it was able to determine the increase of the biodegradability of the CWHPO effluent. Zahn-Wellens bioassays of the CWHPO effluent reached a biodegradability of ca. 60% after 17 days as compared to the negligible biodegradation of as-received wastewater. Although this biodegradability is lower than that obtained by the sucrose solution, used as highly biodegradable control sample, this value is close to the threshold described in literature for considering a wastewater biodegradable (c.a. 70%) [38]. In agreement with Zahn-Wellens bioassays, the $\text{BOD}_5$/COD ratio after the CWHPO treatment increased from 0.07 to 0.13. Therefore, although the CWHPO effluent cannot be considered completely biodegradable, the mixture of this effluent with a highly biodegradable urban wastewater would be an interesting alternative for co-treatment the CWHPO effluent.

3.2. Integrated CWHPO-RBCs treatment

Prior to the integration of CWHPO with RBCs, the latter biological treatment was operated for 10 weeks under continuous feeding of a synthetic municipal wastewater with a hydraulic retention time of 8.75 h. The organic loading rate was 2 g$_{\text{TOC}}$/day·m$^2$ with an inlet stream of ca. 100 mg/L of TOC concentration. Figure 5 shows TOC concentration of the inlet and outlet streams along the acclimation time, where it can be seen the high stability of the system. During that period of time, TOC removals higher than 90% were achieved, whereas the reduction of the COD was 77%, as it is seen in Table 2. Additionally, the oxidation of the nitrogen nutrients was also attested.
Figure 6 depicts the TOC concentration of inlet agrochemical wastewater (2), CWHPO effluent (3), RBC feed (4) and RBC treated effluent (5) along the operation time for the three percentages of the CWHPO effluent in the RBC feed (2.5, 5 and 10 % v/v). The TOC profiles evidenced a high stability of the performance of both chemical and biological processes. For the lowest percentage (2.5 % of CWHPO effluent and 97.5 % of the simulated municipal wastewater), the TOC conversion was ca. 55 % after the CWHPO and 66 % after the subsequent RBCs. These results indicate a good adaptation of the aerobic microorganisms for the by-products of the CWHPO effluent, which accounts for ca. 53.6 % of the TOC content of the inlet RBC stream. Thus, it is remarkable that RBCs are able to biodegrade not only the TOC fraction of the simulated municipal wastewater but also part of the TOC loading of the CWHPO effluent. As the percentage of the CWHPO effluent in the RBCs feed was increased a remarkable enhancement of the TOC removal was observed (71 % and 78 % of TOC removals for 5 and 10 % of the CWHPO effluent, respectively). Note that mixing percentages of 5 and 10 % correspond to TOC loadings coming from the treated agrochemical wastewater of 70 % and 83 % of the overall TOC content in the RBC feed. Thus, there is no doubt of the successful performance of the RBC for the treatment of a non-biodegradable agrochemical wastewater previously treated by CWHPO to reduce the organic loading and to increase its biodegradability. These results are in clearly agreement with the \( \text{BOD}_5/\text{COD} \) ratio and the Zahn Wellens bioassays of the CWHPO effluent.

Additionally, other parameters such as COD, nitrates, nitrites, total nitrogen, sulphates and pH were determined in the final streams of integrated CWHPO-RBC treatments for 5 % and 10% of the CWHPO effluent in the RBC feed. Table 3 summarizes the characterization data of the RBC feed and treated effluent at the pseudo-steady state.
This pseudo-steady state was characterized by constant effluent characteristics measured in terms of TOC and COD when three consecutive readings had variation less than ± 10% [40]. COD removals were also improved as the percentage of the CWHPO effluent in the RBC feed increased (71 and 80 % for the 5 and 10 % of the CWHPO effluent in the RBC feed, respectively). For the nitrogen compounds, it was observed an increase of the NO$_3^-$ and NO$_2^-$ concentrations. Likewise the overall total nitrogen (TN) content decreased during the biological treatment (55 % and 49 % for the 5 % and 10 % of the CWHPO effluent in the RBC feed, respectively). These results indicate both autotrophic nitrification of the nitrogen sources via ammonium oxidation and heterotrophic denitrification of nitrite and nitrate. The nitrites/nitrates produced in the outer aerobic biofilm layer could diffuse into deeper anoxic layers of the biofilm and there, they could be reduced in parallel with ammonium oxidation. Consequently, nitrification may occur on the surface of the biofilm, while denitrification would take place in the inner layers of the biofilms as anoxic part of the RBCs where the oxygen diffusion is limited along the thickness of the biofilms [32, 41].

Finally, it must be point out that the final effluents taken from the CWHPO-RBC system comply all the monitor parameters of the Spanish legislation that regulates the discharge of liquid industrial effluents to the sewage system: COD (401 mg/L), pH (7.7-7.9), TN (58 mg/L) and SO$_4^{2-}$ (107 mg/L).

4. Conclusions

An agrochemical wastewater has been successfully treated by coupling of heterogeneous CWHPO and RBCs. It has been demonstrated that the heterogeneous CWHPO may be part of a process train for increasing the biodegradability of an agrochemical wastewater. The CWHPO process was able to convert the non-
biodegradable compounds of the as-received wastewater into oxidized by-products which are more amenable to be biologically degraded by the consortia of RBCs. In the integrated CWHPO/RBCs process, the RBC system was fed with 2.5, 5 and 10 % in volume of the CWHPO effluent. The highest percentage of CWHPO effluent showed a remarkable performance of the RBCs with TOC and TN reductions of 78 % and 49 %, respectively. Moreover, a high stability was also proven by RBCs for the co-treatment of a simulated municipal wastewater with up to 10 % of the CWHPO effluent.

Acknowledgements

The authors thank “Comunidad de Madrid” and European Social Fund through the Project S2009AMB-1588 and the Spanish Ministry of Science and Innovation for the financial support through the project Consolider-Ingenio 2010 CSD2006-044 and for funding José Ángel Siles López through Project CTM2005-01293 and Grant BES-2006-14074. Authors also thank ACAI Depuracion S.L. (Huesca, Spain) for the transfer of the RBC.

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