Removal of Oxyfluorfen from polluted effluents by combined Bio-Electro processes

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Highlights

- Low oxyfluorfen concentrations were completely removed by means of bioprocesses.
- When operating with high oxyfluorfen concentrations product inhibition appeared.
- Electrochemical treatment completely removed the non-biodegraded fraction.
- Coupling biological and electrochemical processes ensure oxyfluorfen mineralization.
- Na₂SO₄ as supporting electrolyte increased the first order rate in about 20%.

Abstract

In this work, the combination of biological and electrochemical processes to mineralize oxyfluorfen has been studied. First, an acclimatized mixed-culture biological treatment was used to degrade the biodegradable fraction of the pesticide, reaching up to 90% removal. After that, the non-biodegraded fraction was oxidised by electrolysis using boron-doped diamond as the anode. The results showed that the electrochemical technique was able to completely mineralize the residual pollutants. The study of the influence of the supporting electrolyte on the electrochemical process showed that the trace mineral solution used in the biological treatment was enough to completely mineralize the oxyfluorfen, resulting in total organic carbon removal rates that were well-fitted by a first-order model with a kinetic constant of 0.91 h^{-1} . However, the first-order degradation rate increased approximately 20% when Na₂SO₄ was added as supporting electrolyte, reaching a degradation rate of 1.16 h^{-1} with a power consumption that was approximately 70% lower.

46 **Keywords**

47 Herbicide; biological treatment; electrochemical treatment; combined process; boron-
48 doped diamond

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1. INTRODUCTION

In recent years, environmental pollution has become a serious problem in our society. Pollution affects natural waters, which can be polluted with different chemicals, such as heavy metals, inorganic salts, and organic solvents. Currently, some of the most hazardous and persistent pollutants released into the environment, pesticides and herbicides, come from agricultural activities. The world's largest agricultural producers and exporters, the EU, Brazil, USA, and China are some of the world's largest pesticide users – each using 827 million, 831 million, 1.2 billion, and 3.9 billion pounds of pesticides in 2016, respectively (Donley, 2019). Unfortunately, pesticides and herbicides not only pollute soils but are also widely present in surface water and groundwater (Nguyen et al., 2014; Chair et al., 2017a). Moreover, these pollutants can be transported away from their application points by air or rain, causing environmental and health problems to humans and animals far away from their application points (Chair et al., 2017b). For these reasons, it is necessary to develop technologies that can completely remove these chemicals from the environment (Fontmorin et al., 2012; Carboneras et al., 2018).

Oxyfluorfen is a commonly used herbicide that is manufactured to destroy herbaceous plants and prevent their development in agricultural activities. It is a diphenyl-ether herbicide used for broad spectrum pre- and post-emergent control of annual broadleaf and grassy weeds with a variety of tree fruit, nut, vine and field crops (Vieira dos Santos et al., 2017).

Currently, biological treatment is the most widespread method for wastewater treatment. Biological treatments possess important advantages because they are cost effective, well studied, and can be easily adapted to local needs (Liu et al., 2010; Ganzenko et al., 2014). In the literature, biological treatments have been reported

extensively for biotechnological transformation, dehalogenation, removal of aromatic compounds, etc. (Basha et al., 2009). Also, some authors have suggested biological treatments for the same purpose using pure or mixed cultures (De Lucas et al., 2007; Saez et al., 2012; Briceño et al., 2016; Castillo Diaz et al., 2016). In these studies, it has been reported that biological reactors operated with mixed cultures achieved even higher removal efficiencies than those operated with pure cultures (Fernandez-Morales et al., 2010; Briceño et al., 2016). Mixed cultures employ undefined consortia of organisms that develop based on ecological selection principles (Fernandez et al., 2008; Fernandez et al., 2010). This approach is very interesting not only because of the greater flexibility to exposure to different pollutants but also because of its reduced operating costs. Unfortunately, bioprocesses are not applicable when dealing with substrates containing refractory or recalcitrant chemicals such as those present in commercial herbicides (Salles et al., 2010; Fontmorin et al., 2013). In the literature, some researchers have studied the removal of these refractory pollutants using advanced oxidation processes (AOPs). An AOP is based on the generation of $\cdot\text{OH}$ radicals; these radicals are some of the most powerful oxidizing agents (Barrera-Díaz et al., 2014). Examples of AOPs include photodegradation, electro-Fenton and electrochemical oxidation. Electrochemical techniques also have disadvantages. The main limitation is their high energy consumption to obtain complete mineralization, in the range of 100 to 150 kWh kg⁻¹ COD, (Ganzenko et al., 2014) and therefore their relatively high economic costs (Liu et al., 2010; Oller et al., 2011). Due to the limitations and advantages of both technologies, biological and electrochemical, a good solution is to combine the low cost of biological treatments with the effectiveness of electrochemical processes.

Biological and electrochemical processes can be combined in different ways for the treatment of wastes. If biological oxidation is applied as a pre-treatment, the objective is to remove the biodegradable COD fraction. Usually, this configuration requires a long acclimatization period (Carboneras et al., 2017). Conversely, if the electrochemical process is used as a pre-treatment, most of the pollutants will be eliminated or transformed into more biodegradable compounds that subsequently could be oxidized in the biological treatment. When working with the latter configuration, the higher biodegradability of the effluent minimizes the acclimatization period of the microbial culture used in the biological treatment (Fernandez et al., 2011) but increases the energy consumption and therefore the treatment costs. Anyway, different authors have reported very high efficiencies of the electrolysis when using boron-doped diamond (BDD) to remove persistent pollutants (Liu et al., 2010; Barrera-Díaz et al., 2014). The lower cost of the combination of a first biological pre-treatment and a subsequent electrochemical treatment was considered very convenient and was the option selected in this work. In this context, the aim of this study was to evaluate the coupling of a biological and an electrochemical advanced oxidation process for the removal of a commercial pesticide based on oxyfluorfen, focusing on the compatibility of both treatments and on the influence of electric conductivity of biologically treated wastes on the performance of the electrochemical treatment, both in terms of removal efficiency and operational costs.

2. MATERIALS AND METHODS

2.1 Microbial mixed culture development and commercial reagent

The seed used to grow the microbial mixed culture was collected from an oil refinery wastewater treatment plant. The seed was grown by feeding Bushnell-Haas Broth (BHB) culture media (Simarro et al., 2012), and 200 mg L⁻¹ of oxyfluorfen was used as the sole carbon source. The acclimatization stage was carried out under aerobic conditions. To ensure oxygen availability, the batch reactors were open to the atmosphere (De Lucas et al., 2005). The homogeneity of the liquid bulk was obtained by a magnetic stirrer rotating at 150 rpm. The temperature was controlled during the acclimatization stage at 20 °C by means of a laboratory incubator. The acclimatization was carried out in the dark to prevent any photocatalytic degradation and growth of algae. After an acclimatization period of 7 months, the planktonic microbial mixed culture developed was able to degrade oxyfluorfen.

Oxyfluorfen is commercialised under different brand names. In this work, the commercial product Fluoxil® was used. In addition to oxyfluorfen, Fluoxil® also contains xylene, cyclohexanone and calcium dodecylbenzenesulfonate as a surfactant. These molecules help to solubilize oxyfluorfen.

2.2 Biological pre-treatment

A series of experiments was carried out in 500 mL bioreactors containing different concentrations of oxyfluorfen, ranging from 85 to 500 mg L⁻¹, at different operational temperatures ranging from 15 to 30 °C. In the literature similar concentrations of pesticides have been used (Carboneras et al., 2018). To avoid trace mineral limitations during the bio-treatments, the mineral solution BHB was added to the bioreactors. As inoculum, 5 mL of acclimatized bacterial culture was added to each reactor. The batch

reactors were continuously mixed by a magnetic stirrer rotating at 150 rpm, operated at four different temperatures: 15, 20, 25 and 30 °C, and kept in contact with the atmosphere to ensure oxygen transfer to the liquid bulk. To ensure reproducibility, all experiments were performed in triplicate.

2.2 Electrochemical treatment

Electrolysis of the effluent obtained in the biological pre-treatment was carried out in a single-compartment electrochemical flow cell (Diacell[®] 101, WaterDiam) described elsewhere (Carboneras et al., 2018). A BDD electrode was used as the anode, and a stainless-steel electrode was used as the cathode. The electrodes were circular with a geometric area of 78 cm². Effluent circulation was maintained through the cell using a peristaltic pump at a flow rate of 15 mL s⁻¹. The electrical current was applied using a power supply (FA-376 PROMAX), and the temperature was kept constant by means of a recirculating water bath. Three different current densities were studied: 10, 30 and 100 mA cm⁻². Due to the presence of the mineral solution required for the biological degradation of the pollutant, the BHB medium, electrolysis experiments were carried out without the addition of an external electrolyte support. Once the electrochemical tests were finished, a final test adding Na₂SO₄ was carried out to compare the performance of the electrochemical process when operating with and without Na₂SO₄ as the supporting electrolyte. A diagram of the experimental setup used for the electrolysis is shown in Fig. 1.

1. Bulk tank
2. Peristaltic pump
3. Electrochemical reactor
4. Heating bath
5. Power supply

Figure 1. Electrochemical setup.

2.3 Analytical techniques

The measurements of oxyfluorfen were performed by high-performance liquid chromatography (HPLC). The biomass growth was determined by direct optical density (OD) measurements at 600 nm using a spectrophotometer (Stevenson et al., 2016). Previously, a calibration between the OD and the volatile suspended solids concentration was carried out. Moreover, internal calibrations were performed to ensure the accuracy of the biomass concentration measurements. The determination of total organic carbon (TOC) was performed using a Multi N/C 3100 Analytik Jena analyser. Measurements of pH and conductivity were carried out by using probes. With regard to the biomass characterization, a MALDI-TOF AXIMA Assurance by Shimadzu was used. The matrix solutions were prepared by saturating α -cyano-4-hydroxycinnamic acid in a 1:48:2 acetonitrile:water:trifluoroacetic acid matrix solution. Then, the microorganisms were sterilized using ethanol at 75%, and the solution was centrifuged at 1000 rpm for ten minutes. After centrifugation, the supernatant was removed, and the biomass recovered from the precipitate using 20 μ L of an acetonitrile/formic acid/water (50:35:15) solution according to the procedure described in the literature (Mateo et al., 2016).

3. RESULTS AND DISCUSSION

As stated above, this work is focused on the removal of a commercial herbicide solution by combining biological and electrochemical treatments. In this research, the biological process was the first step, followed by an electrochemical step, because of its economical advantages. Below, the main aspects of both treatments are presented.

3.1 Biological treatment

Previous research has demonstrated the existence of a lag phase when halogenated pesticides are biodegraded (Carboneras et al., 2017). For this reason, a previously acclimatized bacterial culture was used in this work. The acclimatized bacterial culture was characterised by the MALDI-TOF technique. The results show that the culture was a mixture of 5 different species: *Achromobacter denitrificans*, *Achromobacter xylosoxidans*, *Pseudomonas putida*, *Pseudomonas oryzihabitans* and *Brevibacterium casei*. In the literature, *Achromobacter* has been related to the biodegradation of pesticides (Xu et al., 2013; Akbar and Sultan, 2016) and *Pseudomona* genera has been described as able to degrade chlorinated pesticides in general (Nawab, 2003). Finally, *Brevibacterium* has been related to the removal of pesticides, insecticides, etc. (Tang and You, 2012; Jariyal et al., 2015; Sabourmoghaddam et al., 2015).

With regard to oxyfluorfen removal, the biological treatment was performed at 4 different temperatures (15, 20, 25 and 30 °C). Fig. 2 presents the influence of the temperature on the biological removal of oxyfluorfen when the initial concentration was 500 mg L⁻¹. Similar results were obtained when performing biodegradation at different temperatures. This observation was ratified by fitting an exponential decay model to all the experimental results. From this fitting, it was observed that the correlation coefficient of all the experimental data was approximately 0.93. Moreover, it is important to highlight that any 95% prediction band of the experimental data series

covered almost all the experimental observations. These results indicated that when removing oxyfluorfen, the influence of the temperature on the biological removal of oxyfluorfen was negligible within the range studied. As shown in Fig. 2, at the studied temperatures, a significant degradation of the initial oxyfluorfen was achieved, removing approximately 90% of the initial pesticide concentration in all cases.

Figure 2. Oxyfluorfen concentration trends during the biological pre-treatment at different temperatures (initial concentration 500 mg L⁻¹). The light grey area represents the 95% prediction band, and the dark grey area corresponds to the 95% confidence band.

From the fitting of the experimental data, it was observed that the biodegradation constant rate was 0.12 h⁻¹. It is also important to highlight that the remaining oxyfluorfen concentration at the end of the biodegradation stage was similar regardless of the temperature used (approx.. 54 mg L⁻¹). A similar behaviour has been reported in the literature (Zhang et al., 2018). This residual oxyfluorfen concentration could be

explained in terms of an inhibition experienced by the long term exposition of the microbial culture to the pesticide.

Both explanations depend on the concentration of the toxic agent. Therefore, with the aim of determining the influence of the concentration on the biodegradation of the herbicide, different initial concentrations were studied. Fig. 3a presents the obtained results for different initial concentration of the pesticide (85-500 mg L⁻¹ at a constant temperature of 30 °C).

Figure 3. a) Oxyfluorfen and b) biomass concentration evolution during the biological pre-treatment at 30 °C.

As seen in Fig. 3a, when working with 350 and 500 mg L⁻¹, an initial exponential removal trend was observed, the removal rate drastically decreased after approximately 20 h. In addition to the change in the removal trend, it was observed in all cases that the increase in the oxyfluorfen concentration led to an increase in the residual oxyfluorfen concentration. According to the literature (Chen et al., 2008; Castro-Villalobos et al., 2012), this behaviour indicates a sort of inhibition. In any case, a significant pesticide removal, of at least 85%, was reached in all cases in spite of the initial pesticide concentration. To better comprehend the pesticide removal by the microbial culture, Fig. 3b presents the evolution of the biomass concentration during the biodegradation process. This allows to estimate the biomass growth rate, which initially follows an exponential trend regardless of the initial oxyfluorfen concentration. Thus, it can be

concluded that the observed inhibition is due by the accumulation of poisoning degradation products (Probst et al., 2015). This was supported by the decreasing average biomass yield when the oxyfluorfen concentration increased, which decreased from 1.16 mg biomass mg⁻¹ oxyfluorfen when operating at a concentration of oxyfluorfen under 150 mg L⁻¹ to 0.71 and 0.66 mg mg⁻¹ when operating at concentrations of 350 mg L⁻¹ and 500 mg L⁻¹ of oxyfluorfen, respectively.

In the literature, it has been stated that the biological degradation of oxyfluorfen transforms the nitro group into an amino group. The amino group can be subsequently acetylated to N-[4-(2-chloro-4-trifluoromethyl-phenoxy)-2-ethoxy-6-hydroxy-phenyl]acetamide (Zhao et al., 2016). Additionally, the ether bond of the intermediate metabolite can be broken (Zhang et al., 2018), yielding 2-ethoxy-4,6-dihydroxy-phenyl]acetamide and 2-chloro-4-trifluoromethylphenol that can be further catabolized by dechlorination to 4-trifluoromethyl-phenol (Chakraborty et al., 2002; Keum et al., 2008).

With the aim of accurately comparing the performance of the biodegradation process when operating at different initial concentrations, a product inhibition-based mathematical model Eq. (1), as described in the literature (Roels, 1983), was fitted to the experimental data as follows:

$$r_S = q_{max} \cdot \frac{C_S}{K_S + C_S} \cdot \frac{K_P}{K_P + C_P} \cdot X \quad (1)$$

where

r_s is the biodegradation rate

q_{max} is the maximum biodegradation rate

C_S is the substrate concentration

C_P is the product concentration

K_S is the substrate half saturation constant

K_P is the product inhibition constant

X is the biomass concentration

The mathematical model was simultaneously fitted to all the data series, obtaining the following fitting values: $q_{\max}$ 0.6 (mg g⁻¹ biomass h⁻¹), K_S 24.9 (mg L⁻¹) and K_P 137.1 (mg L⁻¹). The correlation coefficient was higher than 0.93 in all cases, indicating a good fit of the model to the experimental data series. The good fit indicates that the final concentration of the pesticide at the end of the experiments can be explained by the product inhibition kinetics based on non-competitive inhibition (Roels, 1983). To obtain additional information about the amount of organic matter contained in the water after the biological treatment, the total organic carbon (TOC) content was measured. The TOC content provides information about the presence of degradation intermediates. The obtained results are presented in Fig. 4. Fast biological removal of TOC was observed during the first hours, and the removal rate then slowed. Finally, the TOC content was kept constant, indicating that the microbial culture was not able to completely mineralize the pollutants. As previously stated from the data presented in Fig. 3a, almost 90% of the oxyfluorfen was removed. However, the mineralization achieved was approximately 70% according to the TOC results presented in Fig. 4, which indicates the accumulation of biodegradation intermediates or the low degradation of components in the initial formulation of Fluoxil®.

Figure 4. TOC content evolution during the biological pre-treatment at 30 °C.

Because of the presence of persistent pollutants after the biodegradation stage, an electrochemical post-treatment was proposed with the aim of fulfilling the complete mineralization of the pollutants contained in the wastewater.

3.2 Electrochemical treatment

Once the biological treatment was finished, the electrochemical oxidation of residual oxyfluorfen and the intermediates accumulated during the biological pre-treatment of the herbicide were studied. The tests were performed by feeding the effluent generated by the biological pre-treatment carried out with an initial concentration of 500 mg L⁻¹ at 30 °C. This effluent contained approximately 60 mg L⁻¹ of oxyfluorfen, which was the remaining herbicide concentration at the end of the biodegradation process. This effluent was selected because of its complexity, contained biodegradation intermediates but also some oxyfluorfen.

In the first step of the electrochemical treatment, no additional supporting electrolyte was added because of the presence of trace minerals, the BHB medium, required for previous biological treatment. The influence of the current density was first studied. Figure 5 shows the evolution of the oxyfluorfen concentration with the applied electric charge at different current densities (10, 30 and 100 mA cm⁻²). The initial pH was 7.2, and the initial conductivity 383 μS cm⁻¹.

Figure 5. Evolution of the oxyfluorfen concentration during electrolysis with BDD at 10, 30 and 100 mA cm⁻² current density.

As shown in Fig. 5, the complete depletion of oxyfluorfen was achieved in all cases, although the electric charge required slightly depended on the current density applied: approximately 22 Ah L⁻¹ in the case of working at 10 mA cm⁻² and approximately 26 and 35 Ah L⁻¹ in the case of using 30 and 100 mA cm⁻² respectively. The increase of the electric charge required when increasing the current density applied could be explained by the inefficiencies and side reactions taking place when operating at high current

densities (Llanos et al., 2019).

As in the case of the biological pre-treatment, the TOC content, pH and conductivity were monitored. With regard to TOC removal, its final concentration was undetectable in all cases, confirming the complete mineralization of the herbicide oxyfluorfen and all the intermediates generated in the biological process. In all cases, the conductivity and the pH were approximately constant during electrolysis. The pH was maintained at 7.0 ± 1.0 , and the conductivity was maintained at approximately $400 \pm 100 \mu\text{S cm}^{-1}$. These results support the fact that the coupling of biological and electrochemical processes is a promising technology for complete removal of oxyfluorfen from wastewater with lower costs.

Finally, an additional experiment was carried out with the aim of evaluating the performance of the electrolysis when adding the most common supporting electrolyte, Na_2SO_4 . To do that, 0.035 M Na_2SO_4 was added to the effluent from the biological step before the electrolysis test, presenting the solution an electric conductivity of 220 mS cm^{-1} . The objective of this test was to determine whether the addition of a conventional supporting electrolyte enhanced the electrolysis of the biological effluents. This comparison is important because the biological effluent contains a significant amount of ions due to the addition of the trace minerals of the BHB medium used as a nutrient source. In Fig. 6, the results obtained are presented.

Figure 6. Influence of the electrolyte nature on the TOC during the electrolysis of oxyfluorfen solutions at 30 mA cm^{-2} with and without Na_2SO_4 .

In Fig. 6, for the same applied charge, the TOC removal when adding $0.035 \text{ M Na}_2\text{SO}_4$ was slightly faster than that when only the BHB nutrient solution was present because of the high ionic strength and conductivity of the Na_2SO_4 . The results of both electrochemical treatments, with and without Na_2SO_4 , were fitted by a first-order model (Govindaraj and Pattabhi, 2015). The first-order rate constant obtained was 0.91 h^{-1} when operating with BHB and was 1.16 h^{-1} when Na_2SO_4 was added. From the comparison of the degradation rates when operating with BHB and Na_2SO_4 , it can be stated that an increase in the first-order removal constant of approximately 20% was obtained when adding Na_2SO_4 as the supporting electrolyte. The better results obtained when operating with Na_2SO_4 can be explained by the persulfate generation during

electrolysis (Barrera-Díaz et al., 2014). In comparing the values of the cell voltage and the product of these voltages by the specific current charge passed, the improvements in the power consumption from adding small amounts of Na_2SO_4 can be better seen. For example, for a removal of 90% of the TOC, an applied charge of 18 Ah L^{-1} was required when operating only with BHB medium, and 12 Ah L^{-1} was required in the case of adding Na_2SO_4 . Being the current efficiencies 15% for the experiments carried out with BHB and 22% when adding Na_2SO_4 . In terms of power consumed, when operating only with BHB medium it was consumed 360 kWh m^{-3} and when adding Na_2SO_4 it was consumed 122 kWh m^{-3} . These values are lower than those expected when applying electro Fenton, about 1250 kWh m^{-3} . Anyway the final cost of a full scale plant could be drastically influenced when scaling the process due to the surface requirements for the electrolysis process. Taking into account that the cell voltage decreased from 20 to 10.2 V when adding Na_2SO_4 , the power consumption decreased by approximately 70%, which is a large reduction in the power consumption when adding Na_2SO_4 .

4. CONCLUSIONS

This study has demonstrated that the sequential combination of a biological and electrochemical processes allowed for the complete removal of the oxyfluorfen pesticide. Its treatment in a biological reactor is able to degrade up to 85% at a maximum removal rate of $48.9 \text{ mgL}^{-1}\text{h}^{-1}$. However, the accumulation of poisoning degraded products start to inhibit the biodegradation after 20 h of treatment. At this stage, electrochemical combustion on BDD can effectively continue the treatment from the effluent of the electrochemical treatment without requiring the addition of extra amounts supporting electrolyte. Notwithstanding, Na_2SO_4 could be added to the electrolysis medium in order to accelerate the degradation process (up to 20%) and reduce the energy requirements (70% approx.) from about 360 kWh m^{-3} to about 122 kWh m^{-3} .

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