Is it worth using ultrafiltration as a pre-concentration stage for the treatment of oxyfluorfen by electrochemical BDD oxidation?

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Abstract

The present work deals with the use of ultrafiltration as a pre-concentration stage in the electrochemical degradation of a non-polar organochlorine compound (oxyfluorfen) with boron-doped diamond (BDD) anodes. The first stage of the work consisted in evaluating the performance of a pilot scale ultrafiltration unit to concentrate a solution of a commercial formulation of oxyfluorfen (Barre®) at total recirculation mode. The ultrafiltration membrane exhibited a total rejection of oxyfluorfen, around 70 % rejection of TOC and a permeate flux of $285.1 \text{ L h}^{-1} \text{ m}^{-2}$ at 4 bar and 25 °C. The rejection of oxyfluorfen is higher than expected due to the presence of surfactant compounds in the commercial formulation selected, what promotes a mechanism of micellar enhanced ultrafiltration. Next, a discontinuous ultrafiltration test was performed, maintaining this high rejection of oxyfluorfen and observing a limited contribution of fouling mechanisms, according to the adjustment of the data to fouling models. Regarding the electrochemical oxidation of the concentrate with BDD anodes, it was observed an increase in the specific power consumption from 590 kWh kg^{-1} for the raw solution to 882 kWh kg^{-1} for the concentrate. This unexpected result can be explained due to the limited rejection of the soluble fraction in the ultrafiltration stage, what produced a lower concurrence of oxidants in the electrochemical oxidation step. According to these results, it can be stated that it is worth using ultrafiltration as a concentration stage for commercial formulations of non-polar organochlorines with both high rejection and flux, although it should be combined with degradation technologies different from electrochemical oxidation.

Keywords: ultrafiltration; oxyfluorfen; non-polar organochlorine; BDD; electrochemical oxidation

Highlights:

- Oxyfluorfen (as commercial Barre®) is efficiently concentrated by ultrafiltration
- Oxyfluorfen rejection of 1 and permeate flux of $285.1 \text{ L h}^{-1} \text{ m}^{-2}$ are obtained
- Models predict a limited occurrence of fouling phenomena in the concentration stage
- The effect of current density in oxyfluorfen and TOC degradation is studied
- Ultrafiltration does not decrease the energy needed for oxyfluorfen degradation

1. Introduction

Pollution caused by human activities, such as industry and agriculture is a major concern that requires novel techniques to deal with the increase of persistent contaminants in soil and water [1-3]. The use of herbicides in developed countries is an essential part of agricultural production, as it is aimed to improve indirectly the crop yield by killing or inhibiting the growth of weeds that might compete with the desirable main plant for nutrition, light and water [4]. Nevertheless, it is well known that the use of this chemical compounds is associated with significant undesirable impacts in the environment and in human health [5]. To face this problem, many technologies have been developed and tested to remove this kind of compounds from synthetic and real water effluents, including physical, chemical and biological processes [6, 7].

Among the processes developed for the treatment of wastewater containing herbicides, electrochemical degradation of pollutants in water presents high efficiency and include cathodic dechlorination, electrocoagulation, electro-Fenton technologies and anodic oxidation, mainly employing boron-doped diamond (BDD) electrodes [8-11]. In this context, one of the priorities is to improve the efficiency of electrochemical technologies when facing the treatment of diluted streams, since the performance of these processes is deeply affected by mass transfer limitations under these conditions [12-14]. One of the solutions to overcome these limitations is to pre-concentrate the contaminants and, after this process, use a

1 conventional electro-oxidation technology to remove the pollutants from water. In previous
2 works of our research group regarding the treatment of non-polar organochlorines, the pre-
3 concentration stage was successfully performed by electrocoagulation, showing a clear
4 decrease in the energy consumption required when coupling the concentration technology
5 with electro-oxidation or electro-Fenton [15, 16].

6
7 Membrane technologies represent an additional group of processes that can be applied to pre-
8 concentrate the pollutants prior to their degradation by electrochemical technologies. Several
9 works have demonstrated the viability of coupling nanofiltration or reverse osmosis with
10 electrochemical oxidation in order to efficiently degrade organic pollutants [17-19].

11
12 In the present work, the applicability of ultrafiltration as a pre-concentration stage to treat a
13 commercial formulation of oxyfluorfen (a non-polar organochlorine pesticide) is proposed.
14 The use of ultrafiltration, instead of nanofiltration or reverse osmosis, allows working with a
15 higher permeate flux and thus lower area requirements. After the concentration stage, the
16 concentrated stream was submitted to an electro-oxidation step with BDD anodes. The
17 performance of the ultrafiltration membranes to concentrate oxyfluorfen was evaluated,
18 including the rejection of oxyfluorfen and TOC and the occurrence of concentration
19 polarization and fouling phenomena. Next, the electro-oxidation of oxyfluorfen (EO) with
20 BDD anodes was studied, evaluating the effect of current density in the degradation of both
21 oxyfluorfen and TOC. Finally, the effect of the pre-concentration stage in the specific power
22 consumption needed to degrade oxyfluorfen by EO was evaluated.

23 24 **2. Materials and methods**

25 26 27 *2.1. Chemicals*

28 Oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene) is a
29 hazardous organochlorinated diphenyl-ether compound that has been used as herbicide with
30 a low solubility in water (0.116 mg L⁻¹) and low vapor pressure (0.026 mPa at 25 °C), and
31 acts as a selective pre- and post- emergent contact herbicide to control certain annual

1 broadleaf and grassy weeds [20]. Additionally, its biological effects both on plants and
2 mammals have been documented, and its main effect consists of cell membrane damage since
3 it inhibits protoporphyrinogen oxidase, a precursor of protoporphyrin IX, a molecule that is
4 related with hemoglobin and chlorophyll function [21].

5 Due to its low water solubility this oxyfluorfen must be mixed with other compounds, such
6 as surfactants, in order to be properly used. For this reason, the synthetic wastewater used in
7 this study was prepared with a commercial formulation of the pesticide, Barre® which was
8 provided by a local store named Jovenes Agricultores. Apart from oxyfluorfen, (24%), the
9 mixture contains Solvent naphtha (petroleum) > 25%, and Cyclohexanone < 15%). Sodium
10 sulfate anhydrous (>99%) and sulfuric acid (96%) were obtained from Panreac. Deionized
11 water (Millipore Mili-Q system) was used to prepare all solutions.

12 13 *2.2. Analytical techniques*

14
15 To determine the efficiency of the system proposed, total organic carbon (TOC) and
16 oxyfluorfen concentration were monitored. TOC was measured using a Multi N/C 3100
17 Analytic Jena analyzer and the evolution of oxyfluorfen concentration during the
18 experiments was assessed through high permeation liquid chromatography (HPLC) coupled
19 to a Phenomenex Gemini 5 μm C18 and a mixture of acetonitrile/water (70:30 (v/v)) as
20 mobile phase at $0.3\text{ cm}^3\text{ min}^{-1}$ and a detection wavelength of 220 nm was selected keeping
21 the temperature of the oven at 25 °C. Aliquots of 20 μL were injected. The oxyfluorfen
22 detection limit was 0.2 mg dm^{-3} . Prior to each analysis, all samples were filtered using a 0.22
23 μm nylon filter (Scharlau, provided by Scharlab).

24 25 *2.3. Experimental setup*

26 27 *2.3.1. Ultrafiltration pilot-scale plant*

28
29 The ultrafiltration device used in the present work was a cross-flow pilot scale ultrafiltration
30 plant with a recirculation loop fully described elsewhere {Llanos, 2009 #307}. Basically, it
31 consists of a 100 L stainless steel feed tank, from which the ultrafiltration ceramic membrane

1 is fed by two pumps, one recirculation pump and one feed pump. The ultrafiltration module
2 consists on a stainless steel Mini Kerasep (Novasep) with axial exits which consists of a
3 ceramic multitube membrane formed by 19 channels ($D_h = 3.5$ mm), 38 cm length and 25
4 mm external diameter and a filtration area of 0.0816 m^2 . The employed membrane consists
5 of a 15,000 Da cut-off and it is formed by a monolithic support of $\text{Al}_2\text{O}_3 - \text{TiO}_2$ and a TiO_2
6 active layer.

7 8 *2.3.2. Electro-oxidation in concentrated feed of oxyfluorfen*

9 Electro-oxidation (EO) was carried out using a Boron Doped Diamond (BDD, Adamant
10 Technologies, Switzerland) electrode as anode and a stainless-steel electrode (AISI 304) as
11 cathode under different current densities (500, 250 and 50 A m^2). Both electrodes were
12 circular (geometric area of 78 cm^2 and an electrode gap of 9 mm), placing the concentrate
13 oxyfluorfen solution from the ultrafiltration assays in a glass tank (0.6 dm^3) and circulated
14 through the electrolytic cell by means of a centrifugal pump at a flow rate of $2.5 \text{ dm}^3 \text{ min}^{-1}$.
15 Electrolysis were carried out in galvanostatic mode and the pH was not controlled during the
16 experiments.

17 18 *2.4. Experimental procedure*

19 20 *2.4.1. Ultrafiltration*

21 To characterize the behavior of the ceramic membrane used in the present work, the first step
22 consisted of one test at total recirculation mode (permeate being circulated to the feed tank),
23 for increasing transmembrane pressures from 0 to 4.5 bar. In these tests, the cross flow
24 through the ultrafiltration module was maintained constant in 2000 L h^{-1} . The temperature
25 was monitored and the values of the permeate flux corrected to 25°C based on the viscosity
26 of the solution. Samples were obtained from the permeate and the feed tank to calculate the
27 rejection coefficient of both oxyfluorfen and TOC.

28 Next, to obtain an oxyfluorfen concentrate, a second test at discontinuous mode (permeate
29 being conducted out of the system) was performed. In this case, 80 L of a 100 mg dm^{-3}
30 oxyfluorfen solution was placed in the tank of the pilot scale plant, keeping the

transmembrane pressure at a constant value of 4 bar. This test was carried out throughout a period of 2 h.

2.4.2. Electro-oxidation

The experimentation began with the cleaning of the experimental setup which consists in the polarization of the electrochemical cell with H₂SO₄ 20% followed by a rigorous rinsing with miliQ water. The concentrated phase (2 L containing 234 mg dm⁻³ oxyfluorfen) was then placed into the glass tank and once the current density was set, samples of 15 mL were taken every 10 minutes until the experiment was over.

Current density values ranging from 50 to 500 A m⁻² were applied in order to obtain the best experimental conditions for the higher removal degree. In addition, the influence of the salt addition (1000 mg dm⁻³ of Na₂SO₄) and its effect on the voltage evolution at a current density applied of 500 A m⁻² were evaluated, because these parameters are directly related to the power consumption of the treatment process.

3. Results and discussion

3.1. Concentration step by ultrafiltration

In this section, the results obtained regarding the concentration of oxyfluorfen by ultrafiltration (UF) will be presented. The first step consisted in studying the permeate flux and the rejection coefficient of both oxyfluorfen and TOC using the UF set up described in the previous section, working in total recirculation mode. Figure 1 gathers the influence of transmembrane pressure (ΔP) in permeate flux (J_p , L h⁻¹ m⁻², LHM) and rejection coefficient (R).

Figure 1. Evolution of the permeate (primary axis) and TOC and oxyfluorfen rejection coefficient (secondary axis) in total recirculation assays. ● oxyfluorfen rejection; ▲ TOC rejection; ■ permeate flux. [oxyfluorfen]₀ = 100 mg dm⁻³

Several important conclusions can be obtained from the analysis of Figure 1. The first important one is that the concentration polarization phenomena do not play an important role until reaching a transmembrane pressure higher than 4 bar. Until this value of pressure, the plot of permeate flux vs. transmembrane pressure is almost linear, meaning that the flux is not limited by mass transfer [22].

The second important finding is that the UF membrane selected completely rejects oxyfluorfen. This behaviour is somehow unexpected if the size of the molecule of oxyfluorfen and the pore size of the membrane are compared. The molecule of oxyfluorfen presents a molecular weight of 361.7 Da and an estimated size of 1.23 nm [23], meanwhile the selected UF membrane has a MWCO of 15,000 Da. To explain this unexpected high rejection coefficient, it is necessary to look for rejection mechanisms different from the exclusion of the oxyfluorfen molecules by size.

At this point, it is important to remind that a commercial formulation, which includes chemicals with surfactant behaviour in order to enhance the application of oxyfluorfen to the crops, was used in this study. This allows the molecules of oxyfluorfen to be trapped inside micelles, whose size is much higher than the pore size of the membrane. Thus, the mechanism for the rejection of oxyfluorfen is similar to the technique so-called Micellar Enhanced Ultrafiltration (MEUF)[24-27]. This way, it is possible to reach both higher permeate fluxes

than with nanofiltration or reverse osmosis membranes and high rejection of the target molecule, allowing its efficient concentration by ultrafiltration.

Regarding the rejection of TOC (between 0.6 and 0.7 within the range of pressure selected), it is lower than the rejection of oxyfluorfen. The fraction of TOC that is not rejected may correspond to the soluble fraction of the organics that are included in the formulation of Barre® but are not trapped inside the micelles.

These results at total recirculation mode can be used to characterize the behaviour of the membrane regarding the occurrence of concentration polarization and the rejection of oxyfluorfen. Next, a discontinuous test was performed with two aims. The first one was evaluating the potential role of fouling mechanisms in a real UF concentration test. The second one is producing a concentrated solution that will be further treated by EO.

According to the results obtained at discontinuous mode, the transmembrane pressure was fixed to 4 bar, the maximum value in order to limit the occurrence of the concentration polarization phenomena according to the results presented in Figure 1. Figure 2 shows the results regarding the evolution of permeate flux and oxyfluorfen and TOC rejection with time at discontinuous mode.

Figure 2. Evolution of the permeate (primary axis) and TOC and oxyfluorfen rejection coefficient (secondary axis) in discontinuous test. ● oxyfluorfen rejection; ▲ TOC rejection; ■ permeate flux. [oxyfluorfen]₀ = 100 mg dm⁻³

As it can be observed, the rejection of oxyfluorfen is maintained close to one throughout the entire test. This assures a proper behaviour of UF as a concentration technique and allows the production of a solution free of oxyfluorfen in this stage of concentration. Regarding the evolution of permeate flux, it can be stated that this parameter continuously decreased throughout the test, due to the occurrence of fouling phenomena. This evolution of permeate flux is consistent with the slight increase in the rejection of TOC, as fouling phenomena are caused by physical and chemical interactions between the solutes and the membrane active layer [28, 29], causing both an increase in the rejection and a decrease in the permeate flux produced.

In order to study more in depth the role of fouling phenomena, the evolution of the permeate flux was adjusted to three models, typically used in ultrafiltration systems to characterize the main mechanism of fouling: standard pore blocking (Equation 1); intermediate pore blocking (Equation (2)); cake layer formation (Equation (3)) [30].

a) Standard pore blocking:

$$J_p = J_{po} \cdot \left(1 + \frac{1}{2} K_s \cdot A \cdot J_{po} \cdot t \right)^{-2} \quad (1)$$

b) Intermediate pore blocking:

$$J_p = J_{po} \cdot \left(1 + K_i \cdot A \cdot J_{po} \cdot t \right)^{-1} \quad (2)$$

c) Cake layer formation:

$$J_p = J_{po} \cdot \left(1 + 2 \cdot K_c \cdot (A \cdot J_{po})^2 \cdot t \right)^{-1/2} \quad (3)$$

where J_{po} is the initial permeate flux ($L \cdot h^{-1} \cdot m^{-2}$), K_s the standard pore blocking constant (L^{-1}), K_i the intermediate pore blocking constant (L^{-1}), K_c the cake layer formation constant ($h \cdot L^{-2}$) and A the membrane area (m^2). Figure 3 shows the results of permeate flux together with the adjustment of the three models proposed.

Figure 3. Adjustment of fouling models to permeate flow data in batch mode. ● raw data; ---- intermediate pore blocking; ····· standard pore blocking; -·-·- cake layer formation

As it can be observed, all proposed models predict a similar evolution of permeate flux and adjust the evolution of this parameter with accuracy, a behaviour typical of the systems in which the resistance due to fouling is less than double that of the membrane [31]. This means that the hydrodynamic conditions of the system were properly selected and that the concentration stage could be carried out successfully without a deep contribution of fouling.

3.2. Degradation stage by electro-oxidation

Once the solution containing oxyfluorfen is concentrated by UF, the concentrated stream underwent a process of degradation by electrochemical oxidation. Figure 4 gathers the influence of current density (from 50 A m⁻² to 500 A m⁻²) in the evolution of both oxyfluorfen (Figure 4a) and TOC (Figure 4b) with the applied electric charge.

Figure 4. EO assays of UF concentrated stream. Influence of the current density applied in the removal of oxyfluorfen and TOC: ● $j = 500 \text{ A m}^{-2}$; ■ $j = 250 \text{ A m}^{-2}$; ▲ $j = 50 \text{ A m}^{-2}$. $[\text{oxyfluorfen}]_0 = 234 \text{ mg dm}^{-3}$

As it can be observed in Figure 4a, the efficiency in the degradation of oxyfluorfen increases with the current density. Surprisingly, a different behaviour is obtained in the degradation of TOC as in this case the highest efficiency is obtained for the lowest current density (50 A m^{-2}). This result is again related to the complexity of the initial sample to be treated. As previously commented, the commercial formulation selected has also surfactant and other organic molecules together with oxyfluorfen (petroleum naphtha and cyclohexanone). The higher solubility of surfactant compounds or cyclohexanone (around 90 g L^{-1} at 20°C) makes possible an enhanced transport to the anode surface and its degradation by direct electro-oxidation, which combined with its mediated oxidation by the oxidants produced, allow a higher efficiency in the degradation than that observed for non-soluble molecules as oxyfluorfen [32-34]. This complex scenario may explain the dissimilar performance of the system in degrading oxyfluorfen and TOC, with a higher current density needed for the efficient degradation of the former.

Another important aspect to evaluate the electrochemical degradation of the concentrated stream is the influence of adding an electrolyte to the concentrate stream to improve the degradation in the electrochemical oxidation stage. Thus, Figure 5 shows the influence of adding sodium sulphate on the removal of oxyfluorfen and on the applied potential.

Figure 5. EO assays of UF concentrated stream. Influence of the electrolyte concentration in the removal of oxyfluorfen (a) and in the applied voltage (b) at 500 A m⁻²: ● with and ▲ without electrolyte. [oxyfluorfen]₀ = 234 mg dm⁻³, [Na₂SO₄] = 1000 mg dm⁻³

As it can be observed, adding sodium sulphate has a negligible effect on the efficiency of oxyfluorfen degradation but a marked effect on the applied potential. This result has a direct impact on the specific power consumption (PC) needed to deplete the same amount of oxyfluorfen, represented in Figure 6 for the raw solution (with sodium sulphate added) and for the concentrated solution (with and without sodium sulphate).

Figure 6. Specific energy consumption for the removal of 25 % of oxyfluorfen at 500 A m⁻²: without preconcentration, using UF and Using UF with electrolyte.

1 As it can be observed, the PC required dramatically decreases when adding sodium
2 sulphate to the concentrated solution, due to the marked decrease in the applied potential,
3 gathered in Figure 5. On the contrary, an unexpected result can also be deduced from Figure
4 6: the power consumption required to deplete oxyfluorfen in the concentrated stream is higher
5 than that needed in the dilute stream. This is just the opposite effect than that observed in the
6 degradation of oxyfluorfen previously concentrated by electrocoagulation, as described in
7 our previous works [16].

8 To explain the lower efficiency of the EO system to deplete oxyfluorfen from the
9 concentrated stream, is it important to remind that, in the concentration stage, the rejection
10 of TOC was close to 70%, what means that a fraction of the initial organic matter present in
11 the solution is not retained by the UF membrane. This partial rejection causes that the
12 proportion of some organic molecules of the original mixture in the concentrated stream is
13 expected to be lower than in the original sample. A part of this organic matter that is only
14 partially rejected is the surfactant added to allow the solubilization of oxyfluorfen and
15 enhance its application to the crops.

16 As it has been properly described in previous works, the efficiency in the degradation
17 of non-polar organochlorines is higher in the presence of surfactant [34-36] due to the
18 production of persulphate by Equation 4, produced by the sulphate ions released from the
19 oxidation of the surfactant. If the proportion of surfactant is lower in the concentrated stream,
20 it is expected that the increase in the concentration of oxyfluorfen from 100 mg dm⁻³ to 234
21 mg dm⁻³ is not enough to balance the limited formation of persulphate in the bulk.

26 **4. Conclusions**

27 The two main conclusions of the present work are that ultrafiltration can be efficiently used
28 to concentrate a commercial formulation of oxyfluorfen, combining a high permeate flux and
29 rejection coefficient due to a mechanism of micellar enhanced ultrafiltration. On the contrary,
30 a concentration degree of 2.3 is not enough to decrease the power consumption needed to

deplete oxyfluorfen by electro-oxidation due to the lower proportion of surfactant in the concentrated stream, which hinders the production of persulphate. Moreover, the following specific conclusions can be gathered:

- The ultrafiltration membranes used in the present work reject oxyfluorfen by a mechanism of micellar enhanced ultrafiltration, with a total rejection of this molecule and a permeate flux of $285.1 \text{ L h}^{-1} \text{ m}^{-2}$ at 4 bar and 25 °C.
- It is possible to efficiently concentrated oxyfluorfen by ultrafiltration at discontinuous mode with a limited occurrence of fouling mechanisms as it is predicted by the fouling models applied.
- The efficiency of oxyfluorfen degradation by electro-oxidation increases with current density meanwhile the degradation of TOC follows an opposite trend. This behavior is explained by the complex composition of the initial sample and the contribution of both direct and indirect oxidation mechanisms.
- The specific power consumption needed to deplete the same percentage of oxyfluorfen increase from 590 kWh kg⁻¹ for the diluted solution to 882 kWh kg⁻¹ for the concentrate. This unexpected difference can be attributed to the lower percentage of surfactant in the concentrated stream, which would hinder the production of persulphate.

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