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Efficient treatment of perfluorohexanoic acid by nanofiltration followed by electrochemical degradation of the NF concentrate

Álvaro Soriano, Daniel Gorri, Ane Urtiaga*

Department of Chemical and Biomolecular Engineering, University of Cantabria
Av. de Los Castros s/n. 39005 Santander. Spain

*Corresponding author: urtiaga@unican.es

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Abstract

The present study was aimed at the development of a strategy for removing and degrading perfluorohexanoic acid (PFHxA) from industrial process waters at concentrations in the range 60-200 mg L$^{-1}$. The treatment train consisted of nanofiltration (NF) separation followed by electrochemical degradation of the NF concentrate. Using a laboratory-scale system and working in the total recirculation mode, the DowFilm NF270 membrane provided PFHxA rejections that varied in the range 96.6 to 99.4% as the operating pressure was increased from 2.5 to 20 bar. The NF operation in concentration mode enabled a volume reduction factor of 5 and increased the PFHxA concentration in the retentate to 870 mg L$^{-1}$. Results showed that the increase in PFHxA concentration and the presence of calcium sulfate salts did not induce irreversible membrane fouling. The NF retentate was treated in a commercial undivided electrochemical cell provided with two parallel flow-by compartments separated by bipolar boron doped diamond (BDD) electrode, BDD counter anode, and counter cathode. Current densities ranging from 20 to 100 A·m$^{-2}$ were examined. The electrochemical degradation rate of PFHxA reached 98% and was accompanied by its efficient mineralization, as the reduction of total organic carbon was higher than 95%. Energy consumption, which was 15.2 kWh·m$^{-3}$ of treated NF concentrate, was minimized by selecting operation at 50 A·m$^{-2}$. While most of the previous research on the treatment of perfluoroalkyl substances (PFASs) focused on the removal of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), these compounds have been phased out by chemical manufacturers. Our findings are relevant for the treatment of PFHxA, which appears to be one of the present alternatives to long-chain PFASs thanks to its lower bioaccumulative potential than PFOA and PFOS. However, PFHxA also behaves as a persistent pollutant. Moreover, our results highlight the
potential of combining membrane separation and electrochemical oxidation for the efficient treatment of PFAS-impacted waters.

Keywords: Perfluorohexanoic acid, perfluoroalkyl substances (PFASs), nanofiltration, electrooxidation, boron doped diamond electrode

1. Introduction

Perfluoroalkyl substances (PFASs) are highly persistent organic compounds that contain a fluorinated alkyl chain and a hydrophilic end group (Arvaniti and Stasinakis, 2015). PFASs have been used in a wide variety of applications as part of surfactants, emulsifiers, aqueous film forming foams, additives for polymers, for paper and cardboard coatings used in food packaging products, and for stain and water repellency in textiles and leather, among others (Appleman et al., 2014; Rahman et al., 2014; Yu et al., 2009).

Long-chain PFASs are bioaccumulative and toxic to laboratory animals and wildlife (ECHA, 2014; Lin et al., 2014). Hence, environmental protection institutions have established limits to perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonates with eight or more fluorinated carbons. Perfluorooctane sulfonate (PFOS) and its salts were added to Annex B of the list developed in 2009 as a result of the Stockholm Convention on Persistent Organic Pollutants (Ahrens and Bundschuh, 2014). PFOS and its derivatives were recently added as priority hazardous substances in Directive 2013/39/UE of the European water policy. The United States Environmental Protection Agency has recently set health advisory levels for perflourooctanoic acid
(PFOA) and PFOS in drinking water at 0.07 µg/L, both individually and combined (USEPA, 2016).

Nowadays, industry has phased out the use of PFOA, PFOS, and longer chain homologues (USEPA, 2015). The alternatives are mostly short chain PFASs such as the 6:2 fluorotelomer alcohol (6:2 FTOH), which contains six fully fluorinated carbon atoms (ECHA, 2014). 6:2 FTOH is readily biodegradable, but it degrades into the persistent compounds perfluorohexanoic acid (PFHxA) and perfluoropentanoic acid (L. Zhao et al., 2013). In general, shorter chain PFASs have been reported to be quickly eliminated in mammals (Z. Wang et al., 2015), although PFHxA is equally persistent and cannot be degraded under biotic or abiotic conditions.

Various technologies have been examined for the treatment of PFASs from aqueous media, although most of the previous studies were exclusively focused on the removal of PFOA and PFOS. The most widely studied techniques are adsorption, membranes, and oxidation processes (Arvaniti and Stasinakis, 2015). The use of activated carbon and anion exchange resins was successfully reported for the retention of PFOA and PFOS (Yu et al., 2009; Zaggia et al., 2016; Zhang et al., 2016). Nanofiltration (NF) and reverse osmosis (RO) processes are of special interest in the separation of PFASs from drinking water sources. Several works studied the rejection of PFASs by NF membranes, which ranged from 90% to 99%. Rejections were mainly dependent on the type of membrane, but also on a variety of other factors that included the properties of the solution and the effect of the operating variables (Appleman et al., 2013; Hang et al., 2015; Steinle-Darling and Reinhard, 2008; Tang et al., 2007; T. Wang et al., 2015; C. Zhao et al., 2013). Other studies reported that RO could achieve higher PFASs rejection than NF, which in most cases was better than 99%, but at the expense of significantly lower permeate fluxes (Baudequin et al., 2014; Tang et al.,
2007, 2006). Only a few studies included data about PFHxA rejections by the NF270 membrane (Steinle-Darling and Reinhard, 2008). It is important to note that those studies used artificial or spiked mixtures of PFASs that included PFHxA in low concentrations (1 µg·L⁻¹ and 100-400 ng·L⁻¹), and thus may not reflect mechanisms that dominate at higher PFHxA concentrations similar to those usually found in industrial process streams. Moreover, PFHxA rejection values (> 95%) reported by Appleman et al. (2013) were estimations, as the permeate concentrations were not quantified due to limitations of the analytical technique in the low permeate concentration range.

The use of membrane processes alone is not enough for the overall treatment of PFASs because these compounds are retained in the concentrate stream, which must be treated before disposal. Although the concept of coupling membrane technology with advanced oxidation processes has been previously reported in the treatment of emerging micropollutants such as pharmaceutical compounds in a wide variety of water samples (Dialynas et al., 2008; Ioannou et al., 2013; Pérez et al., 2010; Radjenovic et al., 2011), we are unaware of any studies assessing the impact of its application to the treatment of PFASs.

The strength of the C-F bond makes PFASs resistant to traditional advanced oxidation processes (Sansotera et al., 2014). Electrochemical treatment by anodic oxidation has been examined by several research groups (Chaplin, 2014). Boron doped diamond (BDD) electrodes could satisfactorily decompose the PFOA and PFOS contained in synthetic water solutions (Carter and Farrell, 2008; Ochiai et al., 2011; Urtiaga et al., 2015). BDD electrodes have interesting properties that make their use advantageous for the treatment of organic pollutants. These are their high chemical inertness, hardness, extended lifetime, the ability to generate hydroxyl radicals (HO⁻) from water oxidation, and the efficient use of electrical energy (Cañizares et al., 2005;
Cabeza et al., 2007; Polcaro et al., 2009; Pérez et al., 2010). Most of the research effort is currently focused on the development of new electrode materials (Xue et al., 2015; Yang et al., 2015; H. Zhao et al., 2013; Zhuo et al., 2014) and very little information is available about the electrochemical degradation of PFASs in real polluted water matrixes. Exceptions include the recent study by Schaefer et al. (2015), who demonstrated the electrochemical degradation of PFOA and PFOS in groundwater impacted by the use of aqueous film-forming foams. It is noted that the majority of previous studies have focused exclusively on the removal of PFOA and PFOS. One notable gap is the lack of knowledge about the electrochemical treatment of shorter-chain PFASs that are used in chemical manufacturing processes as alternatives to PFOA and PFOS.

The objective of this work was to study the removal of PFHxA from two process waters produced in an industrial manufacturing process in which the initial concentration of PFHxA was in the range 60-200 mg·L⁻¹. The treatment train began with an initial nanofiltration separation that allowed concentration of PFHxA within the retentate stream. This was subsequently degraded by electrooxidation using BDD electrodes. A commercial BDD electrochemical cell was used. The study of the operating variables that affected the rejection of PFHxA and other salts contained in the process waters was assessed. The effect of the applied current and the mechanisms that govern the kinetics of the electrochemical process are also discussed.
2. Materials and methods

2.1 Water characteristics

Two different samples of process streams produced in an industrial manufacturing process were used in this experimental work. The samples were taken just before the PFHxA collecting facility that removed the contaminant before the general wastewater treatment was applied at the industrial plant. Table 1 displays the chemical characterization of the two samples, referred to as S1 and S2. The main difference lays in the content of PFHxA, which is about three times higher in S1 than in S2. Other components were common inorganic salts, which provided the samples the adequate conductivity for use as an electrolyte in the electrochemical experiments. It can be noticed that the values of total organic carbon (TOC) exceeded the theoretical TOC values calculated from the concentration of PFHxA. Therefore, the industrial waters contained other soluble organic compounds of unknown nature.

In addition to the real process waters described above, model solutions with salt contents equivalent to the real ones were prepared. All chemicals were of analytical grade and used as received without further purification. Perfluorohexanoic acid (≥ 97%) was supplied by Sigma-Aldrich. Calcium sulfate dihydrate (≥ 98%) was purchased from Scharlau. Sodium chloride (≥ 99%) was obtained from Panreac. Sodium carbonate (≥ 99.9%) was supplied by Merck Millipore.

2.2 Nanofiltration experiments

Nanofiltration experiments were carried out in a laboratory membrane cross-flow test cell (SEPA-CF, GE Osmonics). An NF270 flat membrane supplied by Dow Filmtec was used. It is a thin film composite of a polyester non-woven support matrix, a
microporous polysulfone interlayer, and a semiaromatic piperazine-based aromatic polyamide barrier layer. At neutral pH, the NF270 membrane surface is negatively charged, a property that would improve the rejection of large negative species such as perfluorohexanoate, which is obtained by the dissociation of PFHxA at neutral pH (Wang et al., 2016).

The membrane area inside the cell was 155 cm$^2$. New membrane specimens were preconditioned by immersion in ultrapure water for 24 h to 48 h. A back pressure valve (Swagelok, 0-40 bar), installed at the outlet port of the retentate stream, was used to control the operating pressure. The permeate chamber was maintained at atmospheric pressure. The feed was circulated using a diaphragm pump (Hydra-Cell D-03).

Fig. 1 shows the NF set-up. In the total recirculation experiments (Fig. 1a), both the retentate and the permeate streams were continuously recycled to the feed tank. Therefore, in the total recirculation NF experiments the feed composition was constant during the entire experiment. Initially, the NF system was pressurized with the feed solution at 20 bar for one hour with total recirculation of the solution. After achieving stable permeate fluxes in consecutive measurements for at least one hour, the pressure was sequentially reduced to 15, 10, 5, and 2.5 bar. At each pressure, the system was allowed to reach steady-state flux before the next reduction in operating pressure. In concentration mode experiments (Fig. 1b), only the rejection stream was recycled to the feed tank, while the permeate stream was collected in a separate tank. In concentration mode experiments, the concentration of PFHxA and salts in the feed continuously increased during the length of the experimental run. Concentration mode experiments were conducted until a volume reduction factor (VRF) approximately equal to 5 was obtained, where VRF is defined as the ratio between the initial feed volume and the concentrate final volume (Mulder, 1996). In concentration mode, the membrane was
initially pressurized for one hour at 35 bar using deionized water. The pressure was then
fixed at 10 bar during the NF test. In all experiments, the permeate rejection and feed
streams were sampled periodically. All experiments were conducted at room
temperature.

2.3 Electrooxidation experiments

The retentate stream produced in the NF concentration mode tests, which
accumulated PFHxA and soluble salts, was used as the feed solution in the
electrooxidation experiments. The set-up consisted of an electrochemical cell (DiaCell
201 PP, Adamant Technologies), a power supply (Vitecom 75-HY3005D), a jacketed
feed tank, and a cooling bath (Polyscience 9510). The cell contained two parallel flow-
by compartments made of a central bipolar p-Si/BDD electrode and p-Si/BDD anode
and cathode, with an interelectrode gap of 1 mm in each channel. Further details on the
experimental system can be found elsewhere (Díaz et al., 2011; Urtiaga et al., 2014).
The feed tank was filled with 1 L of the NF concentrate, unless otherwise stated. The
experiments were carried out in batch mode, at a constant temperature of 20 °C. Three
different current densities were applied: 20, 50, and 100 A·m⁻². Model solutions
representative of the NF concentrates were used in the experiments aimed at the
selection of the optimum operating conditions for electrooxidation.

To determine the efficiency of the process, it is useful to calculate the specific
electrical charge \(Q, \text{A} \cdot \text{h} \cdot \text{L}^{-1}\) and the energy consumption \(W, \text{kWh} \cdot \text{m}^{-3}\) as follows
(Anglada et al., 2009):

\[
Q = \frac{JAt}{v} \quad (1)
\]
\[ W = QV \] (2)

where \( J \) is the current density (A·m\(^{-2}\)), \( A \) is the total anode area (m\(^2\)), \( t \) is the time (h), \( v \) is the feed tank volume (L), and \( V \) is the cell voltage (V).

The limiting current density \( (J_{lim}, \text{A·m}^{-2}) \) at a given time \( t \), can be calculated as follows (Martínez-Huitle et al., 2015; Panizza and Cerisola, 2009):

\[ J_{lim} = 12Fk_m[PFHxA]_t \] (3)

where \( F \) is the Faraday constant (C·mol\(^{-1}\)), \([PFHxA]_t\) is the concentration of PFHxA (mol·m\(^{-3}\)) at a given experimental time, and \( k_m \) is the mass transport coefficient in the electrochemical reactor (m·s\(^{-1}\)). The factor of 12 is the number of electrons exchanged during the oxidation of one PFHxA molecule. \( k_m \) was calculated following the work of Anglada et al. (2010), who analyzed the effect of hydrodynamics and scale-up for electrochemical cells with a similar geometry to the equipment used in the present study.

2.4 Analytical methods

The perfluorinated compounds were quantified using two different analytical methods. The appropriate method was selected according to the PFHxA concentration range and to the calcium and bicarbonate content in the samples:

1. The PFHxA concentration in the feed and retentate NF samples was generally within the range 5-900 mg·L\(^{-1}\). Moreover, these samples had high calcium, sulfate, and bicarbonate concentrations. High-performance liquid chromatography (HPLC) with a diode array UV-visible detector was employed.
(Waters 2695-DAD). The separation column was an X-Bridge C18 (5 µm, 250 × 4.6 mm). The mobile phase was a solution of methanol (CH₃OH) and sodium dihydrogen phosphate (Na₂H₂PO₄, 20 mM) in the 65:35 volume ratio at a flow rate of 0.5 mL·min⁻¹. The limit of quantification (LOQ) for PFHxA was 5 mg·L⁻¹. The UV absorption at 205.4 nm was used for quantification.

2. HPLC (Waters 2690) equipped with a triple quadrupole mass spectrometer (TQD Detector Acquity, Waters) was used to analyze NF permeate samples, with PFHxA concentrations generally below 5 mg·L⁻¹ and with low salt content. The column was the X-Bridge BEH C18 (2.5 µm, 2.1 × 75 mm). The eluents were: (i) an aqueous solution containing ammonium acetate (CH₃COOHNH₄) 2 mM and 5% of methanol, and (ii) pure methanol. The eluent flow rate was 0.15 mL·min⁻¹. The LOQ for PFHxA was 1 µg·L⁻¹.

It was checked that both analytical protocols provided analogous PFHxA quantification in the feed sample S1.

Conductivity was measured using a portable conductivity meter (Hach sensION 5). The pH was measured using a pH meter (GLP Crison 22). An automatic carbon analyzer (TOC-V CPH Shimadzu) was used to measure the total organic carbon (TOC). The determination of chloride, sulfate, and fluoride anions was carried out by ion chromatography (Dionex ICS-1100) using an ion exchange resin column (Dionex AS9-HC). The mobile phase was sodium carbonate (Na₂CO₃, 9 mM) with a flow rate of 1 mL·min⁻¹. Sodium and calcium cations were determined by ion chromatography (Dionex DX-120) using a Dionex IonPac TM CS12 column and methanesulfonic acid (18 mM at 1 mL·min⁻¹) as eluent.
3. Results and discussion

3.1 Nanofiltration experiments

3.1.1 Total recirculation tests

The volumetric flux of permeate passing through the membrane, $J_v$, is defined by Darcy’s law (Eq. (4)), which states that this variable is the product of the membrane permeability $L_p$ (L·m$^{-2}$·h$^{-1}$·bar$^{-1}$), which is an empirical constant, and the pressure gradient between the two sides of the membrane, defined as the difference between the effective pressure $\Delta P$ (bar) and the osmotic pressure gradient $\Delta \pi$ (bar) (Pérez-González et al., 2015):

$$J_v = L_p (\Delta P - \Delta \pi)$$  \hspace{1cm} (4)

where $\Delta \pi$ is defined as:

$$\Delta \pi = \pi_0 - \pi_p$$  \hspace{1cm} (5)

where $\pi_0$ and $\pi_p$ are the feed and the permeate osmotic pressures, respectively. The osmotic pressure of the solutions was calculated from the concentration of the dissolved salts (Asano, 1998):

$$\pi = 1.19 (T + 273) \sum m_i$$  \hspace{1cm} (6)

where $T$ is the temperature of the solution ($^\circ$C) and $m_i$ is the molality of the constituent in the solution.
Fig. 2 shows the correlation between the permeate flux and the pressure gradient across the membrane. Three types of water samples were considered: ultrapure water, real industrial process waters, and the model solution. The last represents the salt composition of the real samples S1 and S2, according to Table 1, but without the addition of PFHxA. It was observed that the membrane permeability to ultrapure water was highest, \( L_{pw} = 13.3 \pm 0.04 \, \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} \), a value that is similar to previously reported water permeabilities for the same NF270 membrane (Nghiem and Hawkes, 2007). The presence of salts in solution decreased the membrane permeability, as was observed for the flux data obtained with the model solution, \( L_{pm} = 11.7 \pm 1.2 \, \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} \). A similar trend was observed in previous studies dealing with the NF treatment of desalination brines, e.g., Pérez-González et al. (2015) found that solution permeability decreased exponentially when increasing the initial salt concentration. The membrane permeabilities of the two samples of real process water S1 and S2 (which contained PFHxA) were very similar to each other (\( L_{p,S1} = 9.6 \, \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} \); and \( L_{p,S2} = 9.4 \, \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} \)), and lower than the values for pure water and the model salt solution. Hang et al. (2015) reported a similar observation after the nanofiltration of PFOA and suggested that such behavior could be attributed to adsorption of the molecule in the expanded membrane pores.

The effect of the effective pressure gradient on the rejection of PFHxA and ions was also studied. The observed rejection \( (R_{obs}) \) was calculated as follows (IUPAC, 1996):

\[
R_{obs} = \left( 1 - \frac{c_p}{c_r} \right) \times 100
\]  
(7)
where \( C_p \) and \( C_r \) are the concentration of the species in the permeate and retentate streams, respectively.

Due to the high solvent flow through the membrane and the high rejection of the species, solutes accumulated on the membrane surface. Thus, the actual solute concentration at the membrane surface was higher than in the bulk solution, known as the concentration polarization phenomenon. In order to calculate the real membrane rejections \( (R_{\text{real}}) \) the equation of Fujioka et al. (2012) was employed:

\[
R_{\text{real}} = \frac{R_{\text{obs}} \exp \left( \frac{L}{k} \right)}{1 + R_{\text{obs}} \left[ \exp \left( \frac{L}{k} \right) - 1 \right]} \times 100
\]

(8)

where \( k \) is the mass transfer coefficient of the considered species (m·s\(^{-1}\)). \( k \) was calculated using Eq. (9), which is valid for laminar flow through rectangular closed channels (van den Berg et al., 1989):

\[
Sh = \frac{2hk}{D_{AB}} = 0.664 \cdot \frac{Re^{0.5}Sc^{0.33}}{L} \left( \frac{2h}{L} \right)^{0.33}
\]

(9)

In Eq. (9) \( Sh \), \( Re \), and \( Sc \) are the Sherwood, Reynolds, and Schmidt numbers, respectively; \( h \) is the NF cell channel height (1.7 mm) and \( L \) is the length of the path that follows the fluid inside the NF cell (0.13 m). \( D_{AB} \) is the diffusion coefficient of the species in water (m\(^2\)·s\(^{-1}\)). The diffusion coefficients reported by Samson et al. (2003) were applied for the ionic species (sulfate, calcium, sodium, and chloride). In the case of PFHxA, the Wilke-Chang equation (Perry et al., 1997) was used to estimate its diffusion coefficient in water, \( D_{PFHxA,w}=7.05 \times 10^{-10} \) m\(^2\)·s\(^{-1}\), at 25ºC.
The dependence of the PFHxA real rejection on the effective pressure is shown in Fig. 3. The PFHxA rejection increased from 97.3% to 99.1% for S1, and from 96.6% to 99.4% for S2 in the range of effective pressure gradient $2.4 < (\Delta P - \Delta \pi) < 19.9$ bar. Two main observations can be derived. First, the PFHxA real rejection remained high over the entire range of applied pressure. Secondly, the difference in the concentration of PFHxA, which was three times higher in S1 than in S2, did not significantly affect the rejection percentage. Appleman et al. (2013) reported PFHxA rejections higher than 95%, when using the same NF270 membrane for the treatment of spiked artificial groundwater with a feed PFHxA concentration of 1 $\mu$g·L$^{-1}$. The authors revealed that PFHxA was not detected in the permeate over the limit of quantification of the analytical technique used in that work. It can be argued that the differences in the feed concentration, which in the study of Applemann et al. (2013) was 200 times lower than in sample S1 of the present study, significantly reduced the concentration gradient across the membrane and thus the permeation flux of the species. Similar observations were reported by Steinle-Darling and Reinhard (2008) who studied the nanofiltration of synthetic mixtures of 15 perfluorochemicals in deionized water with concentrations in the range 150-400 ng·L$^{-1}$. So far, to the best of our knowledge, the present study is the first one reporting the NF of PFHxA in real industrial process waters. Past research (Bellona and Drewes, 2007) demonstrated that NF membranes achieved a high rejection of negatively charged organic compounds through electrostatic exclusion. However, the detection of PFHxA in the permeate observed in the present work suggests that once the compound reached a partitioning equilibrium at the feed/membrane interface—which is enhanced by the high feed concentrations used in this work—the diffusion mechanism governs the overall solute transport through the membrane pores.
Fig. 4 shows the real rejection of ions (sulfate, chloride, sodium, and calcium) as a function of the operating pressure for the sample S1. Similar rejections were observed when NF was applied to S2 and to the model solutions (results not shown). In the range of operating pressures studied, chloride rejection increased from 6.8% to 56.4%, sodium rejection from 65.6% to 88.2%, calcium rejection from 87.3% to 97.9%, and sulfate rejection from 98.8% to 99.6%. The high values of sulfate rejection are very similar to those obtained for PFHxA because both are large negatively charged species that are easily rejected by the negatively charged membrane at neutral pH. The low value of chloride rejection can be explained by the Donnan ion distribution between the solution and the membrane. It means that sodium and calcium cations were attracted by the negatively charged membrane and were highly distributed from the liquid phase to the membrane phase. Chloride ions, which are much smaller than sulfate anions, tended to pass through the membrane together with the cations in order to preserve the electroneutrality (Hilal et al., 2015). Similar ion rejection behavior was observed by Pérez-González et al. (2015), who treated brackish water desalination brines in the pressure range of 5 to 20 bar using the same NF270 membrane. The observed ions rejections were beneficial for increasing the conductivity of the concentrate to be used as an electrolyte in the electrochemical treatment.

### 3.1.2 Concentration mode experiments

The purpose of the concentration mode experiments was to obtain a low volume of highly concentrated PFHxA solution. In addition, these experiments allowed the evaluation of the stability of membrane performance along the time of operation in terms of PFHxA rejection and permeate flux. Fig. 5 shows the evolution of the permeate flux over time (for samples S1 and S2) using a feed pressure of 10 bar. In both cases the flux slightly decreased in the first hours and then stabilized at a constant value. The
membrane permeability values at constant flux were $L_{p,S1}=9.4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and $L_{p,S2}=8.6 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, which are similar or only slightly below those reported in the above section. At the end of each experiment, the membrane was tested again with ultrapure water to evaluate whether the observed loss of permeability corresponded to reversible or irreversible fouling. For example, after the NF test with S1, the membrane permeability to pure water was $12.8 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, which was only 4% less than the initial value reported in Fig. 1. The difference is believed to be due to the variability of properties in different membrane specimens. It was concluded that the NF of PFHxA solutions did not generate irreversible fouling in the NF270 membrane.

In the concentration mode experiments, the NF270 membrane showed high PFHxA real rejections that were essentially constant over time: 98.2 ± 0.2%, and 98.8 ± 0.2%, for S1 and S2 respectively (real and observed PFHXA rejection values with time are compared in Figure S1 of the supplementary material). The volume was reduced from the 10 L initially used as feed, to a final volume of approximately 2 L of concentrate. PFHxA concentrations of 870 mg·L⁻¹ and 344 mg·L⁻¹ were achieved in the final concentrates C-S1 and C-S2, respectively. The evolution with time of the PFHxA concentration in retentate and permeate streams is given in Figure S2 of the supplementary material. Simultaneously, the conductivity of the concentrates reached 2.48 mS·cm⁻¹ and 2.63 mS·cm⁻¹. These concentrates served as feed for the next electrooxidation step. PFHxA was detected in the permeates at concentrations of 21 mg·L⁻¹ for S1, and 8 mg·L⁻¹ for S2. These values corresponded to the composite permeates obtained throughout the duration of the tests. Moreover, Fig. 6 shows that under the conditions of the present study, PFHxA concentrations in the permeate and in the retentate matched a linear relationship ($r^2=0.97$), an observation that further supports
diffusion as the predominant PFHxA transport mechanism through the NF270 membrane.

3.2 Electrooxidation experiments

3.2.1 Influence of the applied current density

Initial tests aimed at the selection of the applied current density were performed using model solutions (CM-S1) that were prepared with similar PFHxA concentrations and salts composition as the NF concentrates obtained from sample S1. Fig. 7 depicts the development of PFHxA and TOC with time at three applied current density values: $J_{\text{app}}=20$, 50, and 100 A·m$^{-2}$. The kinetics of PFHxA degradation and mineralization were clearly enhanced when the applied current density was increased from 20 to 50 A·m$^{-2}$. Further increase in current density to 100 A·m$^{-2}$ provided an additional improvement in degradation kinetics, although less noticeable than in the previous jump from 20 to 50 A·m$^{-2}$.

The recent review by Niu et al. (2016) proposed that electrochemical oxidation mechanism of PFCAs involves electron transfer to the anode to form the highly reactive $\text{C}_n\text{F}_{2n+1}\text{COO}^-$ radical, which then reacts with electrogenerated hydroxyl radicals. According to this pathway, PFHxA degradation would include both direct and indirect electrochemical oxidation steps. BDD anodes are well known for their wide electrochemical window that allows the formation of hydroxyl radicals at lower electrode potentials than those needed for the oxygen evolution reaction. However, as hydroxyl radicals are confined to the proximity of the anode surface, two different operating regimes can be defined for BDD oxidation: i) when the applied current density is below the limiting current density, the electrolysis is under current control and the concentration of organic compounds decreases linearly with time; ii) when the
applied current density is above the limiting current density, the electrolysis is under
mass transport control and the removal of organics follows a first-order exponential
trend. In the present study, the limiting current density ($J_{\text{lim}}$, Eq. (3)) was calculated as
$J_{\text{lim}} = 48.1 \text{ A} \cdot \text{m}^{-2}$ at the initial PFHxA concentration in CM-S1. This means that when
working at $J_{\text{app}} = 20 \text{ A} \cdot \text{m}^{-2}$, the electrolysis was initially under current control but
rapidly shifted to mass transfer control at $t = 1 \text{ h}$ as the concentration of PFHxA
decreased. When $J_{\text{app}} = 50 \text{ A} \cdot \text{m}^{-2}$, the system was working under mass transfer control
for the entire experiment. The small but noticeable increase in the PFHxA removal rate
observed at $100 \text{ A} \cdot \text{m}^{-2}$ can be assigned to the oxidative effect of secondary strong
oxidants such as sulfate radicals. This assumption is based on the results reported by
Hori et al. (2005), who found that the photolysis of persulfate anions produced highly
oxidative sulfate radical anions, which efficiently decomposed PFOA and other PFCAs
bearing C$_4$-C$_8$ perfluoroalkyl groups. At present, we are not able to definitely elucidate
the rate limiting step of PFHxA degradation, although the experimental results that
show only a minor kinetic enhancement when the applied current is doubled from 50 to
$100 \text{ A} \cdot \text{m}^{-2}$, point to the predominance of indirect oxidation by means of
electrogenerated oxidants.

To select the suitable operating conditions, it is also useful to look at the evolution of
PFHxA and TOC as functions of the specific electrical charge passed ($Q$), also shown in
Fig. 7. An increase in the applied current density did not significantly affect the efficacy
of the process. The energy demand for 90 % degradation of the initial PFHxA was
calculated using Eqs. (1) and (2). The times for 90% PFHxA reduction were obtained
from the rate constant calculated using the concentration-$Q$ data. Results are
summarized in Table 2, where $V$ is the experimental cell voltage developed under
galvanostatic conditions. The energy consumption for $J_{\text{app}} = 50 \text{ A} \cdot \text{m}^{-2}$ was 15.2 kWh·m$^{-3}$,
the lowest among the three current intensities under consideration. It was also observed that the electrolysis time needed to reach 90% degradation at 50 A·m$^{-2}$ was three times lower than when the applied current was 20 A·m$^{-2}$. Accordingly, it was decided to select $J_{\text{app}}=50$ A·m$^{-2}$ as the working current density for the electrochemical treatment of the real industrial process concentrates.

The energy consumption for the electrochemical treatment of PFHxA achieved in the present study, 15.2 kWh·m$^{-3}$, is lower than previously reported values for the removal of different PFASs in waters. Zhuo et al. (2011) and Niu et al. (2012) reported the electrolysis of PFOA using tin oxide and lead dioxide electrodes with energy consumptions of 48 and 45 kWh·m$^{-3}$. Similar values in the range 41.7-76.6 kWh·m$^{-3}$ have been gathered by Niu et al. (2016) for the degradation of perfluorodecanoic and perfluorononanoic acids using BDD, SnO$_2$, and PbO$_2$ electrodes. The energy consumption reported in the present study is the lowest of all the values reported so far, which shows evidence of the improvement of efficiency of the electrolysis treatment of PFASs using a pre-concentration strategy.

3.2.2 Electrochemical mineralization of PFHxA in concentrates from industrial process waters.

Fig. 8 shows the development of PFHxA and TOC when treating the real industrial process waters pre-concentrated by NF at the selected value of current density ($J_{\text{app}}=50$ A·m$^{-2}$). Linearized dimensionless values are presented, since the initial concentrations of PFHxA in the two samples were significantly different. The volume of sample is included in the linearization of data because of the lower feed water volume used for C-S2 (0.8 L) than for C-S1 (1 L), due to the lack of sample. After 90 minutes, the degradation of PFHxA concentration was 91% and 98% of the initial in samples C-S1
and C-S2, respectively. It is also interesting to confirm the high removal of TOC, showing the mineralization of the organic compound. PFHxA removal was slightly faster for C-S2 than for C-S1. This behavior can be assigned to its higher initial PFHxA concentration \( \left( C_{0, C-S1} = 870 \text{ mg} \cdot \text{L}^{-1} \right) \). During the experiments we detected degradation products such as perfluoropentanoic acid and perfluorobutanoic acid. In all cases, the observed amounts of secondary PFCAs were lower than the quantification limit of the HPLC-DAD analytical technique. It means that only small amounts of the shorter chain PFCAs obtained upon PFHxA degradation diffused out of the proximity of the anode surface.

Fig. 9 shows the evolution of fluoride with electrochemical treatment. The fluoride concentration reached a maximum at \( t = 90 \) min, and then started to decrease slowly. At the same time, the concentration of calcium decreased continuously, a clear indication that calcium fluoride was being formed from the beginning of the electrochemical test. Local pH variations at the anode and cathode surfaces and the intense fluid turbulence gave rise to the supersaturated calcium fluoride solution and deposition of calcium fluoride on the cathode surface. For electrochemical treatment longer \( 2 \) h, the degradation of PFHxA was nearly completed and there was no further release of fluoride ions. The decrease of fluoride and calcium concentrations was contained showing the slow precipitation of calcium fluoride. Therefore, in the present application, defluorination rate is not an appropriate measurement of the degree of mineralization of PFHxA, as that parameter takes into account the concentration of fluoride ions in the solution. Calcium fluoride scaling was easily removed from the cathode surface by acid cleaning using an aqueous solution of HCl (3 M) at the end of each experimental run. This fouling formation could be detrimental to the performance of the system at larger-scales, which would require implementing a periodical cleaning
procedure to avoid scaling on the electrode surface, as it was recently proposed by Schaefer et al. (2016).

The pseudo-first order kinetic constant for PFHxA degradation obtained from the experimental data in Fig. 8, was 0.0021 m·min⁻¹, after correcting for the volume treated and anode area. This value is ten times higher than the kinetic constant obtained by Niu et al. (2012) for the degradation of PFHxA using a Ce-doped PbO₂ anode. Similarly, Zhuo et al. (2012) reported the electrooxidation of a synthetic aqueous solution of PFHxA (100 mg·L⁻¹) using a small BDD anode (8.5 cm²) in a laboratory-scale batch reactor at an applied current of 232 A·m⁻². In that work, the reported PFHxA degradation kinetic constant was 0.0016 m·min⁻¹. The kinetic constant obtained in the present study surpasses the two previously reported values, and validates the use of commercial BDD cells for the removal of PFASs from industrial process waters.

Fig. 10 shows an overview of the process that combines low pressure nanofiltration as the preconcentration step, and electrooxidation as the degradation technique. This strategy was able to eliminate 90% of the initial PFHxA mass contained in the industrial process waters, at a moderate energy consumption, by increasing the concentration of organic compounds for the electrooxidation process (Sirés et al., 2014). Higher removal rates could be attained by using a more selective membrane system (such as reverse osmosis) that however operates at higher pressures and provides much lower permeate fluxes. Another option would be the electrochemical system alone, which would also be able to further reduce the final PFHxA concentration, at the expense of a higher energy consumption.
4. Conclusions

Results presented herein demonstrate that a combination of nanofiltration (NF) followed by the electrochemical oxidation (ELOX) of the NF concentrate is effective in removing perfluorohexanoic acid (PFHxA) from industrial process waters. Very few previous studies have reported the treatment of PFHxA, and none of them addressed the NF/ELOX conjunction or the concentration range found in industrial streams, thus showing the novelty of the present study.

It is concluded that the NF270 (Dow/Filmtech) membrane provides high PFHxA rejections (reaching 99.6% when operating at a feed pressure of 20 bar), without any noticeable membrane fouling. This performance improves on previously reported results with longer chain PFASs such as PFOA, which showed adhesion to the membrane that reduced the permeate flux. This implies that nanofiltration is a viable technical option for the separation of PFHxA from process water streams when compared to more extended adsorption practices. The presence of sulfate and the adequate rejection of divalent ions by the NF270 membrane provided adequate conductivity to the concentrate stream, which facilitated the subsequent application of electrochemical treatment without the further addition of electrolytes.

Electrooxidation with boron doped diamond electrodes, working at a current density of 50 A m$^{-2}$, easily degraded the PFHxA retained in the NF concentrate. Traces of shorter chain PFASs were observed in the early stages of the electrochemical process, which nevertheless were later degraded below the limit of quantification of the analytical technique. The possible adverse impact of fluoride ions obtained as a final degradation product was avoided by in situ precipitation as calcium fluoride, promoted by the incoming calcium contained in the industrial process stream. The observed kinetics of
PFHxA oxidation was substantially faster than previously reported results using Ce-
thium doped PbO$_2$ and BDD anodes, probably fostered by the optimal selection of operation
variables achieved in this study.

Overall, these results suggest that the process integration of nanofiltration separation
and BDD electrochemical degradation is a promising alternative for the treatment of
PFHxA that could be extended to the treatment of waters impacted by other PFASs such
as PFOA and PFOS.

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Captions

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Table 2. Energy consumption and electrolysis time required to achieve 90% PFHxA degradation in sample CM-S1.

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Figure 1. Nanofiltration set-up in a) total recirculation mode, and b) concentration mode.

Figure 2. Experimental permeate flux data as a function of the effective pressure gradient. Model solution composition: NaCl (60 mg·L⁻¹), CaSO₄ (600 mg·L⁻¹). Averages of duplicate experiments are reported for ultrapure water and the model solution.

Figure 3. PFHxA real rejection as a function of the effective pressure for process water samples S1 and S2 using an NF270 membrane.

Figure 4. Real rejection of ions as a function of the effective pressure. Data were obtained using sample S1 and an NF270 membrane. Similar results were observed for S2 sample and the model solution.
Figure 5. Nanofiltration operation in concentration mode. Permeate flux evolution with time for samples S1 and S2. Feed pressure = 10 bar.

Figure 6. Nanofiltration operation in concentration mode. PFHxA concentration in the permeate vs. PFHxA concentration in the retentate. The NF270 membrane was operated at a feed pressure of 10 bar.

Figure 7. PFHxA and TOC evolution as function of time (t) and specific electrical charge (Q), using the NF concentrate of sample S1: CM-S1 \([PFHxA]_0=774 \text{ mg L}^{-1}\); C-S1 \([PFHxA]_0=870 \text{ mg L}^{-1}\). Initial conductivity=2.31-24.48 mS cm\(^{-1}\). ♦: \(J=20 \text{ A m}^{-2}\); ■: \(J=50 \text{ A m}^{-2}\); ▲: \(J=100 \text{ A m}^{-2}\).

Figure 8. Linearized dimensionless PFHxA and TOC evolution with time using the real concentrates. \(J_{\text{app}}=50 \text{ A m}^{-2}\). ♦:C-S1, \([PFHxA]_0=870 \text{ mg L}^{-1}\), initial conductivity = 2.48 mS cm\(^{-1}\), volume=1 L; ●:C-S2, \([PFHxA]_0=344 \text{ mg L}^{-1}\), initial conductivity = 2.63 mS cm\(^{-1}\), volume=0.8 L.

Figure 9. Calcium and fluoride evolution during the electrochemical treatment of sample C-S1.

Figure 10. Global scheme of the combined NF- electrooxidation process.
Table 1. Main characteristics of the industrial process water samples used in the experimental study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Sample S1</th>
<th>Sample S2</th>
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<tr>
<td>PFHxA</td>
<td>mg·L⁻¹</td>
<td>204</td>
<td>64</td>
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<tr>
<td>TOC</td>
<td>mg·L⁻¹</td>
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<tr>
<td>pH</td>
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<td>Conductivity</td>
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<tr>
<td>Chloride</td>
<td>mg·L⁻¹</td>
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<tr>
<td>Sulfate</td>
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<tr>
<td>Bicarbonate</td>
<td>mg·L⁻¹</td>
<td>98</td>
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<tr>
<td>Calcium</td>
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<td>171</td>
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<tr>
<td>Sodium</td>
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<td>24.9</td>
<td>28.7</td>
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Table 2. Energy consumption and electrolysis time required to achieve 90% PFHxA degradation in sample CM-S1.

<table>
<thead>
<tr>
<th>J_{app} (A·m^{-2})</th>
<th>Kinetic constant k_2 (h^{-1})*</th>
<th>V (V)</th>
<th>Q (A·h·L^{-1})</th>
<th>W (kWh·m^{-3})</th>
<th>Electrolysis time (h)</th>
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<td>20</td>
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<td>100</td>
<td>1.814</td>
<td>16.8</td>
<td>1.27</td>
<td>21.3</td>
<td>0.90</td>
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</tbody>
</table>

* k_2 obtained from the fitting of experimental concentration vs. Q data to \([PFHxA]/[PFHxA]_0 = e^{-k_2 Q}\)
The graphs show the concentration of PFHxS (PFCs) and TOC over time and for different current densities. The concentration decreases with increasing time and current density. The graphs also show the ratio of PFHxS/PFHxS_0 and TOC/TOC_0, which decrease with increasing Q (A h L^{-1}). The data points for J=20 A m^{-2}, J=50 A m^{-2}, and J=100 A m^{-2} are differentiated by color and symbol.
• A combined nanofiltration/electrooxidation process was used to eliminate PFHxA for the first time
• Real industrial process waters were treated.
• NF270 membranes showed PFHxA rejection that reached 99.6% without membrane fouling.
• 98% of PFHxA in the NF concentrate was degraded by BDD electrodes. Mineralization > 95% was achieved
• Electrochemical conditions were optimized for minimizing the energy consumption.