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Feasibility of Micropollutants Treatment by Coupling Nanofiltration and Electrochemical Oxidation: Case of Hospital Wastewater

Abstract: In spite of good performances of the membrane bioreactor (MBR) process, permeate from it can still contain refractory pollutants that have to be removed before water reuse or discharge. The present study is an attempt to combine the advantages of two well-known technologies, which are nanofiltration (NF) and electrochemical oxidation (EO) to treat MBR effluent from hospital wastewater. The concept is based on a preconcentration of micropollutants with a reduction of the wastewater volume by NF and treatment of the NF retentate by oxidation. During filtration process the rejection of ciprofloxacin, as a target molecule, reached beyond 97%. Then the NF retentate was treated by EO using a boron-doped diamond anode (BDD). Galvanostatic electrolyses showed that this anode is efficient to mineralize not only ciprofloxacin but also all the micropollutants and organics contained in MBR effluent. The results demonstrated that rapid mineralization occurred: the removal of total organic carbon and chemical oxygen demand (COD) reached 97% and 100%, respectively, in our conditions in 300 min maximum. The specific energy consumption for the total removal of COD was calculated to be 50 kW h kg⁻¹ COD.

Keywords: antibiotic elimination, nanofiltration, electrochemical oxidation, ciprofloxacin, hospital wastewater

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1 Introduction

It was reported that micropollutants such as pharmaceuticals are widespread in the aquatic environment [1–4]. Because of their limited biodegradability, micropollutants are incompletely eliminated in wastewater treatment plants, whatever the process used: activated sludge treatment or even membrane bioreactor (MBR) process which exhibits good purification performances. As a consequence, refractory pharmaceuticals remain in treated wastewater and are continuously discharged into aquatic systems [3–5]. Considering their persistence and potential long-term toxicity, even at low concentrations, additional treatments are required to prevent their occurrence in aquatic ecosystems and limit the risk of exposed organisms [5–7]. The difficulty in removing these contaminants from waters comes from their resistance to biological degradation, their small size or their extreme dilution. Within the framework of the conservation of the environment and the water resource, it seems necessary besides limiting the discharges of micropollutants, developing new technologies allowing the purification of waters.

In recent works, nanofiltration (NF) and reverse osmosis (RO) have been investigated for the rejection of pharmaceuticals in synthetic solution and surface water [8–11]. Both techniques are considered really efficient to provide pharmaceutical-free treated water. However, they are only separation techniques, and their major drawback is to produce a concentrate stream which contains the pollutants in higher concentration and could be as consequence more toxic than the influent. In this case, concentrate stream cannot be discharged into the environment and its further treatment is necessary.

Electrochemical oxidation (EO) is a promising process for pollutants elimination in particular using a boron-doped diamond (BDD) anode [12–14]. The use of BDD anode allows the production of electrogenerated hydroxyl radicals from water discharge. Because the action of hydroxyl radicals is located close to the

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anode, there are transfer limitations in dilute solution. The coupling of EO with the preconcentration step by NF renders its economically viable.

There are few studies considering the coupling of these two technologies: NF and EO. Pérez et al. [15] investigated EO of RO concentrates using BDD anode. In this study the concentrates were generated from a UF (ultrafiltration)/RO pilot plant which treated the secondary effluent of a wastewater treatment plant. The authors presented the removals of COD, ammonium and 10 emerging pollutants (including caffeine, naproxen and gemfibrozil) from the RO concentrate using different applied current density, ranging from 2 to 20 mA cm⁻². More than 90% of the regular emerging pollutants were removed after 2 h of electrolysis.

To obtain better design treatment strategies and to improve the efficiency of coupling process, further studies are needed. Hospital wastewater which is one of the main sources of micropollutants, especially pharmaceuticals, has never been used for testing the coupling process. Thus, the present work proposed to evaluate the coupling process of NF and EO for the complete elimination of pharmaceuticals which are present in MBR effluent from hospital wastewater. Ciprofloxacin (CIP), a widely used antibiotic, was selected as a target molecule in this preliminary study, because it was found in different wastewater effluents [2, 3, 16] and was also detected in this MBR effluent from hospital. Moreover, NF/EO process was also performed in synthetic solution and a comparison of the performances was done for both matrices.

2 Materials and methods

2.1 Chemicals

The ciprofloxacin ($\geq 98\%$ purity) was purchased from Fluka Company. Physicochemical properties of ciprofloxacin were reported in Table 1. Potassium sulfate ($\geq 99\%$

purity) as supporting electrolyte in EO experiments was analytical grade supplied by Fisher Science. Other chemicals, organics or solvents were high-performance liquid chromatographic (HPLC) or analytical grade.

2.2 Analytical methods

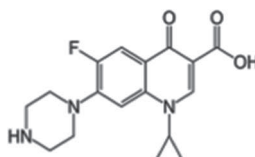
Total organic carbon (TOC) and chemical oxygen demand (COD) were followed during the experiments as global parameters characterizing the total concentration of organics in general. TOC was measured with TOC-V instrument (Shimadzu) and COD was determined by photometry using disposable test tubes (HI93754H-25 LR from HANNA Instruments) and a HACH DR/2400 photometer. TOC and COD detection limits of the equipments used in this study were equal to 0.5 and 3 mg L⁻¹, respectively. At these values, the solution was considered as mineralized, nontoxic and can be rejected in natural water stream. The deviation of TOC was estimated of 2% and 5% for COD.

Concentration of CIP was monitored by high performance liquid chromatography coupled to UV detector (HPLC-UV, Agilent 1200 series) at $\lambda = 276$ nm with a Vydac reverse phase C18 column (5 μ m, 4.6 mm \times 250 mm). The mobile phase of HPLC consisted of a mixture of water: acetonitrile: triethylamine (80:20:0.3 v/v/v) and the pH was adjusted to 3.3 with phosphoric acid. The flow rate was 1.0 mL min⁻¹ and the volume of injection was 20 μ L [19]. With this analysis method, the detection limit of CIP was 0.1 mg L⁻¹. Considering the limitation, to be able to follow CIP elimination in the coupling process, CIP was added in the feed of process both in synthetic solution and MBR effluent.

2.3 NF setup

NF experiments were carried out in a cross-flow filtration unit (Figure 1). The volume of feed tank was 10 L; the

Table 1: Physicochemical properties of ciprofloxacin (CIP).

| CAS number | MW (g mol ⁻¹) | log K _{ow} [17] | pK _a [18] | Water solubility 20°C (g L ⁻¹) | Charge at neutral pH | Chemical structure* |
|------------|---------------------------|--------------------------|----------------------|--|----------------------|---|
| 85721-33-1 | 331.3 | -0.28 | 3; 6.14; 8.7; 10.6 | 30 | Positively charged |  |

Note: *<http://pubchem.ncbi.nlm.nih.gov>.

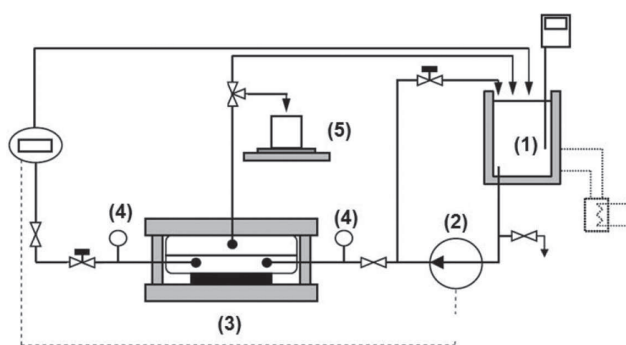


Figure 1: Nanofiltration setup: (1) feed tank (10 L), (2) high pressure pump, (3) cross-flow filtrate cell, (4) pressure monitor, (5) permeate tank (5 L) and balance.

Table 2: Characteristics of membrane NE2540-70.*

| Material | MWCO (Da) | Max. temperature (°C) | Max. pressure (bar) | pH range | NaCl rejection (%) |
|--------------------------|-----------|-----------------------|---------------------|----------|--------------------|
| Film composite polyamide | 250 | 45 | 41.4 | 3–10 | 60–70 |

Note: *Provided by manufacturer: Woongjin Chemical Co., Ltd.

membrane was installed into a stainless cross-flow cell (Sepa CF II, Osmonics) (3) in which the effective membrane area was $1.4 \times 10^{-2} \text{ m}^2$. Concentrate stream was circulated back to the feed tank (1) during experiments; permeate was collected by a vessel (5 L) and the weight was valued by a balance (5) connected to a computer. NE 2540-70 membrane (provided by Woongjin Chemical) was used in experiments. Its characteristics were presented in Table 2.

Membrane was stored in a preservative solution at 4°C (NaHSO_3 0.1 g L⁻¹). It was cleaned by ultrapure water before experiment and installed in the cross-flow cell. Then the compaction was conducted by filtration of ultrapure water at a transmembrane pressure (TMP) equal to 40 bar until a constant flow rate was obtained (around 2 h). Pure water permeability was measured after compaction.

The filtration of CIP solution was taken place at a TMP of 25 bar and a tangential velocity of 0.35 m s^{-1} ($\text{Re} = 416$).

Feed (6 L) was prepared by adding CIP in ultrapure water (as a synthetic solution) and MBR effluent. The initial CIP concentration was 4–5 mg L⁻¹. When the volume reduction factor (VRF) reached 5 in the retentate loop, the experiment was stopped and then the retentate was collected for further EO.

The rejection of the ciprofloxacin by the NF unit was determined at the end of the concentration step ($\text{VRF} = 5$) using eq. (1):

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (1)$$

where C_p and C_f are the concentration of CIP in the permeate and the retentate, respectively. In these conditions permeate and retentate volumes reached were 4.8 and 1.2 L respectively.

2.4 EO setup

The NF retentate was stored in 1 liter thermoregulated glass reservoir (1) and circulated through the electrolytic cell using a centrifugal pump (2) (Figure 2). The flow rate was 366 L h^{-1} . Electrolyses were conducted at 30°C in a one-compartment flow filterpress reactor (3) under galvanostatic conditions. Electrodes were two discs of 63 cm^2 of active surface separated 10 mm. The BDD anode from Adamant was elaborated by chemical vapor deposition on a conductive substrate of silicium. The cathode was a 1 mm thick disc of zirconium. The current was supplied by an ELC AL 924 power supply. As preliminary study all electrolyses were carried out at $\text{pH} = 3$. At this pH the dissolution of CO_2 generated at the anode during electrolysis is negligible. Thus, this pH condition allows avoiding the oxidation of carbonates into percarbonates which decreases the efficiency of the EO. K_2SO_4 (0.1 M) as electrolyte was added in the NF retentate. The applied current density was higher than the limiting current

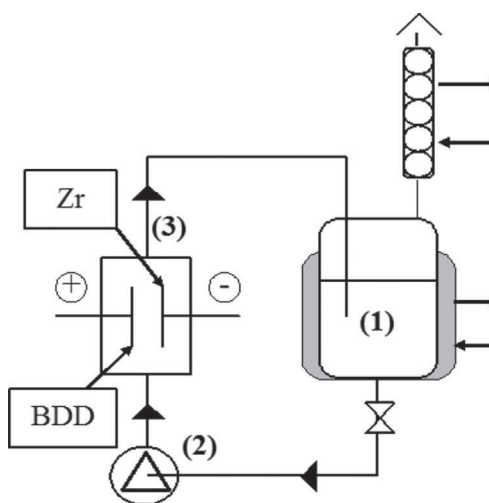


Figure 2: Discontinuous process with a single compartment electrochemical reactor: (1) tank, (2) pump and (3) electrochemical cell.

density, indicating that the process was mass transport controlled. Samples were taken at regular intervals in the tank and the concentration of CIP, TOC and COD were followed.

3 Results and discussion

3.1 NF of ciprofloxacin solution in pure water and MBR effluent matrix

The pure water permeability of the membrane was measured after compaction as $15.8 \pm 1.7 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$. During the filtration, the permeate flow rate was monitored. The filtration was stopped when a VRF of 5 (VRF) was

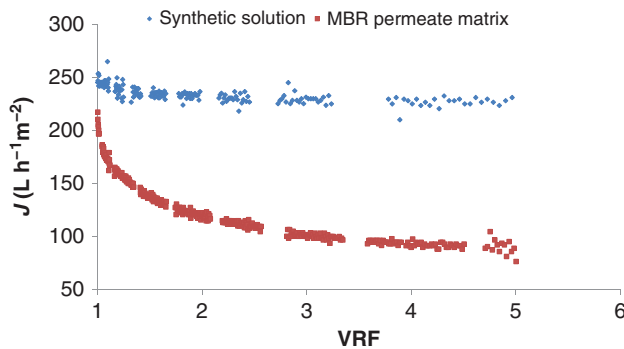


Figure 3: Permeate flow rate during the filtrate of CIP solution in synthetic solution and MBR effluent matrix, feed = 6 L, final retentate = 1.2 L, TMP 25 bar, tangential velocity 0.35 m s^{-1} .

reached in the retentate loop. According to previous studies (results not shown) with the same membrane NE 2540-70 and operating conditions (TMP 25 bar, tangential velocity 0.35 m s^{-1}), permeate flux was $62 \text{ L h}^{-1} \text{ m}^{-2}$ when $\text{VRF} = 5$, while flux was $25 \text{ L h}^{-1} \text{ m}^{-2}$ when $\text{VRF} = 10$ during filtration of MBR effluent. So that $\text{VRF} = 5$ was chosen as the best compromise between keeping favorable NF productivity and reaching high pollutants concentration for EO step.

The permeate flow rate during the filtration is shown in Figure 3. The permeate flow rate in synthetic solution (CIP in ultrapure water) was stable, comparing to the flow rate of MBR effluent which decreased significantly. As a consequence, the filtration in synthetic solution lasted 80 min to reach a VRF of 5 with a stable flow rate from the beginning to the end, while longer experimental time was needed (160 min) to obtain a VRF of 5 during filtration of MBR effluent with a decreasing flow rate. In latter case, results showed that the flux was stabilized at 50% of the initial value. The decrease of flow rate during filtration of MBR effluent was associated with the membrane fouling which was mainly due to deposition or adsorption of organic matter present in MBR effluent.

At the end of the filtration step in MBR effluent matrix, CIP concentration, TOC and COD in permeate and retentate were measured. The results obtained are reported in Figure 4. The global rejection of TOC (R_{TOC}) and COD (R_{COD}) in MBR effluent was 86 and 95%, respectively. CIP rejection (R_{CIP}) was beyond 97% (CIP concentration in permeate was lower than the detection limit of

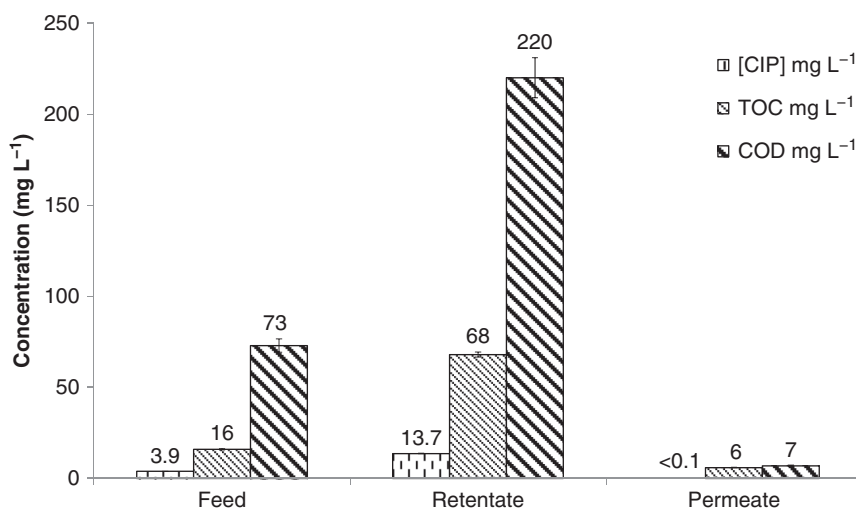


Figure 4: Permeate and retentate CIP concentration, TOC and COD in MBR effluent matrix, feed = 6 L, final retentate = 1.2 L, VRF = 5, TMP 25 bar, tangential velocity 0.35 m s^{-1} .

HPLC), while the rejection in synthetic solution was 87%. It can be assumed that the presence of organic matters in MBR effluent enhanced CIP rejection. This increase can be firstly attributed to membrane fouling which played a role as a second physical barrier to pollutant transfer. Second, it can be expected that specific interactions between CIP and organic matters not only in solution but also in the foulant layer can enhance CIP rejection. Comerton et al. [9] presented similar results on the impact of natural organic matters on the rejection of five endocrine disrupting and pharmaceutically active compounds during NF. These authors presented that the rejection was enhanced due to fouling and the presence of natural organic matters in MBR effluent. In addition, previous researches reported that the influence of foulant layer to the rejection of target molecule depended on the molecule chemical characteristics (hydrophobicity, charge, etc.). In the study of Yangali-Quintanilla et al. [11], alginate foulant layer on NF 200 membrane deteriorated rejections of hydrophilic neutral as well as hydrophilic and hydrophobic ionic pharmaceuticals and endocrine compounds, while rejections of hydrophobic neutral compounds increased. In the present study the opposite result was observed. The target molecule CIP is a hydrophilic and positively charged compound in the experimental condition investigated. Its rejection was enhanced by membrane fouling due to the presence of organic matters. This distinct result was possibly due to the differences of membrane type and foulant layer composition.

Then, the increase of CIP rejection in MBR effluent matrix can be reached in this study due to the fouling occurrence. However, depending on the membrane used the composition of foulant layer, the water matrix and the molecular characteristics of pollutants pollutant rejection can be enhanced or decreased.

Thanks to this high rejection, excellent water quality was obtained from NF permeate, which contained less than 0.1 mg L^{-1} of pharmaceutical target (CIP) and 6 mg L^{-1} of total organic carbon.

The CIP as well as other micropollutants and organic matters in MBR effluent were concentrated into NF retentate which was treated by EO. This concentration step reduces the treated volume and also mitigates the mass transfer limitation which is due to the high dilution in the EO step.

3.2 EO of NF retentate

The NF retentate was transferred directly into the tank (1) of Figure 2. The pH was adjusted and the electrolyte was added before electrolysis. In parallel, an electrolysis of a

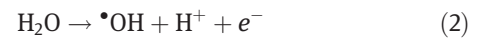
Table 3: CIP concentration, TOC and COD at initial time and at 300 min of electrolysis of synthetic solution and NF retentate in MBR effluent matrix.

| | | CIP (mg L^{-1}) | CIP (mM) | TOC (mg L^{-1}) | COD (mg L^{-1}) |
|---------------------|---------------------|-------------------------------|-------------|-------------------------------|-------------------------------|
| *Synthetic solution | $T=0 \text{ min}$ | 20.6 | 0.062 | 10.2 | 28 |
| | $T=300 \text{ min}$ | 0 | 0 | 1.6 | 0 |
| **NF retentate | $T=0 \text{ min}$ | 11.2 | 0.034 | 62 | 192 |
| | $T=300 \text{ min}$ | 0 | 0 | 1.9 | 0 |

Note: Operating conditions: *synthetic solution: $i = 1.58 \text{ mA cm}^{-2}$ ($i/i_{\text{lim}} = 1.7$), $V = 1 \text{ L}$. **NF retentate in MBR effluent matrix: $i = 7.9 \text{ mA cm}^{-2}$ ($i/i_{\text{lim}} = 1.3$), $V = 1 \text{ L}$.

synthetic solution containing potassium sulfate (0.1 M) and CIP was performed. For both electrolyses, the current density applied was higher than the initial limiting current density. In this case the kinetic regime was under diffusion limitation and the process did not depend on the current density value. Table 3 presents the initial and final values of CIP concentration, TOC and COD obtained during electrolysis of the synthetic solution and of the NF retentate, respectively. This table highlights that 100% of COD removal was reached in both cases. In the same way, the final values of TOC obtained after 300 minutes of electrolysis given in Table 3 are similar and less than 2 mg L^{-1} whatever the initial value (10 or 62 mg L^{-1}) and the matrix (synthetic or real).

Because of its electrochemical properties, BDD anode allows the generation of hydroxyl radical ($\bullet\text{OH}$) resulting from the water discharge by eq. (2). This radical is particularly active to carry out oxygen atoms transfer:



These hydroxyl radicals are physisorbed on BDD surface; therefore they are more available to that chemisorbed on active anodes. Consequently, they react massively close to the electrode allowing the complete mineralization of organic compounds. When the electrolysis is controlled by the mass transfer, COD decreases exponentially with time according to eq. (3) [13]:

$$\text{COD} = \text{COD}_0 \exp\left(-\frac{1}{t}\right) \quad (3)$$

with

$$\tau = \frac{V}{k_d \cdot A} \quad (4)$$

where COD_0 is the initial COD value, τ is a time characteristic of the device, V is the volume of the solution to be

treated (m^3), k_d is the mass transfer coefficient (m s^{-1}) and A is the electrode active area (m^2).

Figure 5 shows a comparison of the normalized COD values obtained during the electrolyses of the synthetic solution and the NF retentate and the COD theoretical values calculated using eq. (3).

It appears that a very good agreement was reached between experiments and theory. Moreover, it was noticed that COD decayed in NF retentate at a faster rate than the theoretical values and the experimental ones obtained in synthetic solution at the end of electrolysis. It can be assumed that a distinct oxidation phenomenon proceeds in addition to EO. With BDD anode, it is possible to generate strong oxidants from anions such as sulfate, carbonate, and chloride which are present into the solution: these oxidants can react chemically with organics. Dong et al. [20] showed that the hydroxyl radicals scavenging by effluent organic matter can be different depending on the wastewater samples.

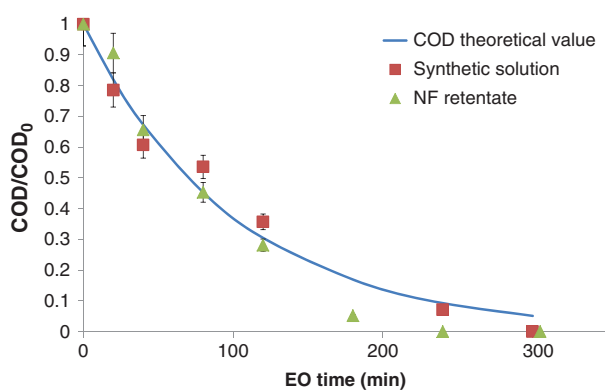


Figure 5: Theoretical (line) and experimental (symbols) normalized COD variation during EO of CIP in K_2SO_4 solution and in NF retentate. Operating conditions: see Table 3.

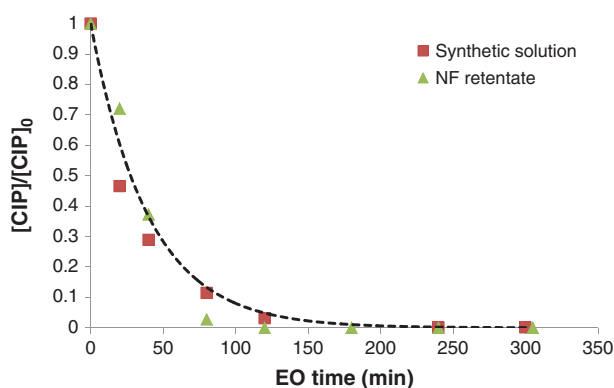


Figure 6: Experimental normalized CIP variation during electrochemical oxidation of CIP in K_2SO_4 solution and in NF retentate. Operating conditions: see Table 3.

Figure 6 shows the variation of the normalized CIP concentration during both electrolyses. A fast and similar CIP concentration decay was observed for both solutions. These trends highlight that a complete removal of CIP was reached in 150 min.

After 300 min, CIP was completely removed, according to the complete removal of TOC and COD. It was also considered that CIP and the other micropollutants contained in NF retentate were completely mineralized in both matrices. The specific energy consumption for the total removal of COD was calculated to be $50 \text{ kW h kg}^{-1} \text{ COD}$. The same complete removal of COD was reached in the study of Pérez et al. [15]. In that research, water matrix was RO concentrate of secondary effluent from a wastewater treatment plant. The specific energy consumption of COD was $59 \text{ kW h kg}^{-1} \text{ COD}$.

4 Conclusions

This study demonstrated the feasibility and high efficiency of coupling NF/EO process as tertiary treatment of hospital wastewater. High rejections were reached in NF step: $R_{\text{CIP}} > 97\%$, $R_{\text{TOC}} = 86\%$ and $R_{\text{COD}} = 95\%$ in MBR effluent matrix. Thanks to this high rejection, it could be expected that both CIP and most of the pollutants were concentrated in retentate.

Pollutants in the retentate were mineralized by EO step, considering 97% of TOC and 100% of COD (good agreement with theoretical value under mass transfer control) were removed.

The global final effluent (NF permeate and EO final tank) contained less than 5 mg L^{-1} of organics.

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References

1. Zuccato E, Calamari D, Natangelo M, Fanelli R. Presence of therapeutic drugs in the environment. *Lancet* 2000;355:1789–90.
2. Chang X, Meyer MT, Liu X, Zhao Q, Chen H, Chen J, et al. Determination of antibiotics in sewage from hospitals, nursery and slaughter house, wastewater treatment plant and source water in Chongqing region of Three Gorge Reservoir in China. *Environ Pollut* 2010;158:1444–50.

3. Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance. *Environ Sci Technol* 2002;36:1202–11.
4. Le Corre KS, Ort C, Kateley D, Allen B, Escher BI, Keller J. Consumption-based approach for assessing the contribution of hospitals towards the load of pharmaceutical residues in municipal wastewater. *Environ Int* 2012;45:99–111.
5. Kümmerer K. Significance of antibiotics in the environment. *J Antimicrob Chemother* 2003;52:5–7.
6. Bruce GM, Pleus RC, Snyder SA. Toxicological relevance of pharmaceuticals in drinking water. *Environ Sci Technol* 2010;44:5619–26.
7. Kümmerer K, Al-Ahmad A. Estimation of the cancer risk to humans resulting from the presence of cyclophosphamide and ifosfamide in surface water. *Environ Sci Pollut Res* 2010;1:486–96.
8. Comerton AM, Andrews RC, Bagley DM, Hao C. The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound a water matrix properties. *J Membr Sci* 2008;313:323–35.
9. Comerton AM, Andrews RC, Bagley DM. The influence of natural organic matter and cations on the rejection of endocrine disrupting and pharmaceutically active compounds by nanofiltration. *Water Res* 2009;43:613–22.
10. Kimura K, Toshima S, Amy G, Watanabe Y. Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. *J Membr Sci* 2004;245:71–8.
11. Yangali-Quintanilla V, Sadmani A, McConville M, Kennedy M, Amy G. Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes. *Water Res* 2009;43:2349–62.
12. Kraft A. Doped diamond: a compact review on a new, versatile electrode material. *Int J Electrochem Sci* 2007;2:355–85.
13. Panizza M, Michaud PA, Cerisola G, Cominellis C. Anodic oxidation of 2-naphthol at boron-doped diamond electrodes. *J Electroanal Chem* 2001;507:206–14.
14. Weiss E, Groenen-Serrano K, Savall A. A comparison of electrochemical degradation of phenol on boron doped diamond and lead dioxide anodes. *J Appl Electrochem* 2007;38:329–37.
15. Perez G, Fernandez-Alba AR, Urtiaga AM, Ortiz I. Electro-oxidation of reverse osmosis concentrates generated in tertiary water treatment. *Water Res* 2010;44:2763–72.
16. Barceló D. *Emerging organic contaminants and human health*, Berlin: Springer, 2012.
17. Reemtsma T, Jekel M. *Organic pollutants in the water cycle: properties, occurrence, analysis and environmental relevance of polar compounds*, New York, NY: John Wiley & Sons, 2006.
18. Qiang ZM, Adams C. Potentiometric determination of acid dissociation constants (pK(a)) for human and veterinary antibiotics. *Water Res* 2004;38:2874–90.
19. Kassab NM, Singh AK, Kedor-Hackmam ERM, Santoro MIRM. Quantitative determination of ciprofloxacin and norfloxacin in pharmaceutical preparations by high performance liquid chromatography. *Rev Bras Ciênc Farm* 2005;41:507–13.
20. Dong MM, Mezyk SP, Rosario-Ortiz FL. Reactivity of effluent organic matter (EfOM) with hydroxyl radical as a function of molecular weight. *Environ Sci Technol* 2010;44:5714–20.