Int. J. Electrochem. Sci., 14 **(2019)** 4409 – 4419, doi: 10.20964/2019.05.21

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Nonylphenol Degradation by Simultaneous Electrooxidation on BDD Anode and Oxidation by H_2O_2 in a Continuous Flow Electrochemical Reactor

M. Rodríguez-Peña, C. E. Barrera-Díaz, B. A. Frontana-Uribe* and G. Roa-Morales*

Centro Conjunto de Investigación en Química Sustentable, UAEM-UNAM, Carretera Toluca-Atlacomulco, Km 14.5, Campus San Cayetano, C.P. 50200, Toluca Estado de México, México.
*E-mail: cbd0044@yahoo.com ; bafrontu@unam.mx;

Received: 18 December 2018 / *Accepted:* 16 February 2019 / *Published:* 10 April 2019

The personal care and hygiene industry, particularly the one dedicated to the production of detergents, generates, among other residues, water with a high concentration of nonylphenol (NP), which is a surfactant that has been classified as an emerging pollutant and reported as an endocrine disruptive chemical. In this study, the use of hydrogen peroxide as an oxidizing agent coupled to an electrochemical process (BDD anodes oxidation) induced elimination of 10% more NP with half the time required for the pure electrochemical process. The integrated process allowed removing 98% of this emerging pollutant. The consumption of energy by the studied integrated technology was low as compared to the electrochemical-ozonation integrated process, showing a reduction in the operational cost and making the proposed process a viable option for the treatment of this kind of waste water.

Keywords: Nonylphenol; degradation; BDD; electrochemical-H_2O_2 integrated process; hydrogen peroxide.

1. INTRODUCTION

Nonylphenol (NP) is a toxic xenobiotic compound classified as an endocrine disruptor capable of interfering with the hormonal system of many organisms. It originates from the degradation of nonylphenol ethoxylates (NPEOs) that are used as industrial surfactants [12]. NPEOs derivatives are a mixture of isomers; the dominant component (approximately 90%) is 4-nonylphenol (4-NP), which bioaccumulates in aquatic organisms at low concentrations [2]. NP can be found in the production and wastewaters of industries that use NPEOs. It is present in paints, adhesives, pesticides, hardeners for epoxy resins, and is used in the production of paper and cosmetic products, as well as in the textile industry [3]. NP has attracted attention due to its bioaccumulation properties, poor bioavailability, and biological characterstics that include carcinogenic, teratogenic, and mutagenic effects; it shows greater estrogenicity than short-chain NPEOs and short chain nonylphenol polyethoxylates (PECN)[4].

NP is in the environment impacting negatively the health of different organisms, affecting the reproductive performance of mammals, fish, and birds, most likely due to its estrogenic, toxic, or combinatorial effects [5]. For example, trout and salmon, are affected in their hormonal system leading to feminization [6]. On the other hand, the xenoestrogenic effect of NP on the male reproductive system has been studied in rodents with testicular apoptosis, reduction in the number of testicular germ cells, sperm abnormalities, and decreased sperm quality, its counting and survival [7]. The effects of NP on brown ducks from Tsaiya in Taiwan, China, have also been studied, showing that relatively large doses of NP can lead to chronic effects on testicular tissues, which sometimes affects spermatogenesis, altering testosterone secretions, and other physiological variables, such as the rate of fertilization [5]. In humans exposure to NP occurs by dermal absorption, inhalation, and ingestion of contaminated food (vegetables) and water [8]. Foods marketed for babies, such as formulas for infants and fruit purees, have been shown to contain high NP concentrations [9]. It has also been detected in human breast milk and body fluids such as serum and urine, and has been shown to cross the human placenta in an ex vivo model of placental perfusion [10,11] Similarly, there is evidence that it affects negatively cell viability and the survival of intestinal cells, inducing cell death and ER stress, as well as down-regulation of the proliferative pathway [8].

Conventional wastewater treatment systems were not designed for these emerging pollutant compounds, and they overcome the treatment without degradation and disseminate into the environment [12]. Biological treatments have been shown to provide low levels of removal, since the NP derivatives contain a branched alkyl chain and the microbial attack on the molecule is not effective [12]. For example, a study on the biodegradation of NP through bacilli in sewage sludge showed a 64.6%-68.3% removal, mainly in the mesophilic phase of composting, with a treatment time of 15 days and high volume aeration [13]. On the other hand, advanced oxidation processes (AOPs) use hydroxyl radicals, strong oxidizing agents, that achieve the degradation of organic compounds fast and almost entirely, transforming the organic compounds into CO_2 and H_2O. It is also possible to transform them into less complex products with low toxicity [14,15]. Degradation of NP by means of AOPs has been achieved, for example, with the use of combined UV/H_2O_2 processes, obtaining a 90% removal in 30 minutes, observing that the degradation of the compound depended on the dose of H_2O_2 in the system [16]. Similarly, ozonation-electrodegradation treatment (O_3-BDD) achieved a 91% NP clearance in 2 hours[17]. The use of an integrated process (degradation is carried out using two complementary techniques), like the last mentioned, has demonstrated that the final operative cost to obtain degradation efficiencies higher than 80% is much less than using only one technique alone [18].

Thus, this report describes the use of a combined treatment with H_2O_2 and electrooxidation on a BDD anode to complete NP degradation. The process is simple to carry out and resulted economically viable for wastewater treatment contaminated with this persistent organic compound.

2. MATERIALS AND METHODS

2.1. Reagents and Chemicals

Deionized water (Millipore Milli-Q system, resistivity: 18.2 mS at 25°C) was used to prepare the synthetic wastewater solutions. 4-Nonylphenol, sulfuric acid (H_2SO_4), and H_2O_2 were used as received.

2.2. Synthetic solution

In this study, a solution of 50 ppm of NP in 0.05 M H_2SO_4 was used in all experiments. The solution was prepared by heating to 70°C and with continuous stirring, until complete dissolution of NP. The volume used in all experiments was 4 L.

2.3. Experimental set-up for the H_2O_2-electrodegradation combined process

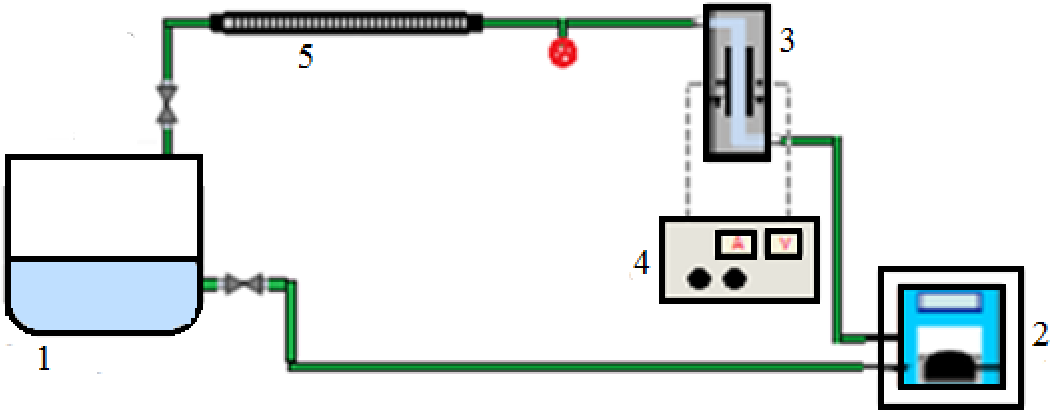

Figure 1. Diagram of the electrochemical treatment. 1, Feed tank (50 ppm of NP in 4 L 0.05 M H_2SO_4. + H_2O_2); 2, peristaltic pump; 3, electrochemical reactor (BDD anode and SS cathode); 4, power source; 5, heat exchanger

The continuous reactor DiaClean® equipped with a DDB/Si electrode as anode and stainless steel as cathode, with a contact area of 70 cm^2 and a distance between them of 0.5 cm was coupled to a system that operates continuously and in a recirculation mode (Fig 1). The treatment began with the nonylphenol solution containing H_2O_2 in the feed tank (HDPE 10 L). The solution of NP is propelled to the electrochemical reactor with a peristaltic pump Masterflex B/T Cole-Parmer, Model 77111-6, working under several flows fitted with Tygone® tubing. The recirculation system was made with drinking water polypropylene quality tubing (Tuboplus®), joined by electrofusion. The electrodes of the reactor were connected to a power source (GW Model GPS-3030D; 1-3A). The temperature of the system was controlled by means of a heat exchanger, which allowed maintaining a constant temperature in the system. Once the solution exited the heat exchanger, it was sent back to the feed tank and recirculated through the system until the experiment was finished. Different H_2O_2 doses were tested during the electrolysis to find the adequate one.

2.4. Analytical procedures

The degradation of NP and the generated intermediates was measured following the behavior of total organic carbon (TOC), using a TOC-L CSN SHIMADZU, and of the chemical oxygen demand (COD), with a Hach DR 5000. COD was determined in all the experiments with COD measurement kits (Hatch 21259 vial digestion, 20–1500 mg L^{-1} range). The consumption of hydrogen peroxide was measured according to the method described elsewhere [19]. After that, COD value was corrected with the value of hydrogen peroxide to obtain the COD associated with the organic pollutant contained in the synthetic water. The behavior of NP and the possible formation of intermediates through degradation was observed with UV-Vis spectroscopy using PerkinElmer spectrophotometer, model Lambda 25, the samples were monitored between 200 and 600 nm, observing at 275 nm the wavelength corresponding to NP. The pH and conductivity were measured using a PHM210 MeterLab and ION 450 MeterLab.

2.5 Equations

The instantaneous current efficiency (ICE) can be used to calculate the apparent Faradic efficiency of COD removal, as follows (Eq. 1) [20].

$$ICE\ (\%) = FV\frac{[(COD_t)-(COD_{t+\Delta t})]}{8I\Delta t} * 100 \qquad (1)$$

where (COD)t and (COD)t+Δt are the COD values ($gO_2 \cdot L^{-1}$) at t and $t + \Delta t$(s), respectively, I is the current intensity (A), F is the Faraday constant (96487 $Cmol^{-1}$), V is the volume of solution (L), and the constant 8 is the oxygen equivalent mass (g $eq.^{-1}$).

The energy consumption of the process under the optimal conditions was calculated by Eq. 2

$$CE\ (kWh) = Volt * Current * time * 1000 \qquad (2)$$

The voltage of the cell was determined by the following expression (Eq. 3)

$$U = \frac{jd}{\Delta} \qquad (3)$$

Where U is the average cell voltage (V), d is the electrode distance (cm), j is the current density (mA cm^{-2}), and Δ is the conductivity of the solution (mS cm^{-1}) [21], the cost of electricity in the USA is US$0.15 per kWh.

$$Cost\ (MXN\$) = kWh * (\text{US\$/kWh}) \qquad (4)$$

3. RESULTS AND DISCUSSION

3.1. Optimal dosage of hydrogen peroxide

NP degradation was attempted by means of electrochemical oxidation using a BDD anode in the presence of H_2O_2. To follow the disappearance of the contaminant and the formation of intermediates, aliquots of the treated solution were spectrophotometrically monitored between 200 and 600 nm during electrolysis. Diverse amounts of H_2O_2 were used, which allowed determining the adequate dose for a fast degradation. Figure 2 shows the spectrum obtained during the electrochemical treatment of NP using 1.0 mL $H_2O_2L^{-1}$. After adding the adequate dose of H_2O_2 to the system, the absorbance at 275 nm increased with respect to that obtained with raw water (NP and distilled water). After 5 minutes, the spectrum shows the absence of the surfactant characteristics, having an asymptotic behavior. There is a hypochromic effect in the absorbances, approaching the baseline, so that we can conclude that after 60 min an almost complete disappearance occurred. Likewise, it was observed that the same spectrum was present at 180 min and 120 min, so that 2 hours seemed to be sufficient for the degradation of the compound. The spectra obtained after 120 min with different doses of oxidant (0.5, 1.0, and 1.5 mL $H_2O_2L^{-1}$) showed faster degradation with the higher concentrations, indicating that the interaction between the oxidant and the NP is fast and facilitates degradation.

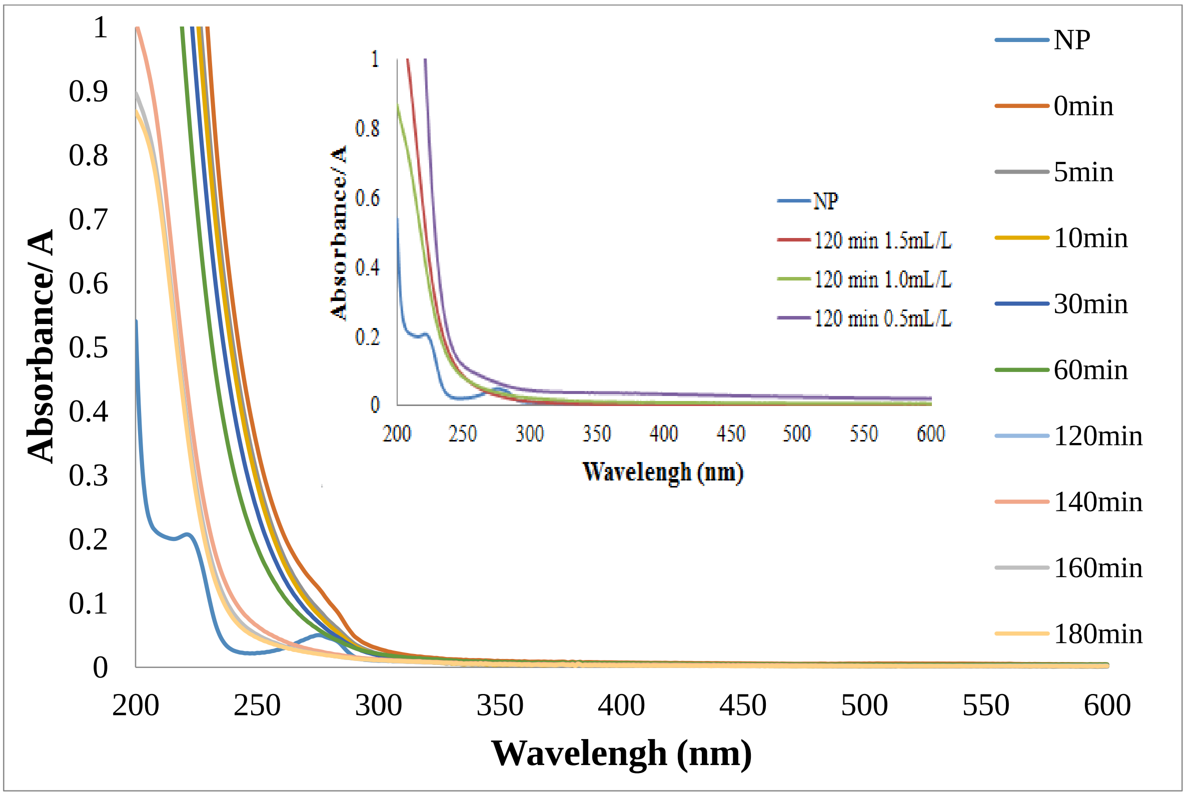

Figure 2. UV–Vis curves of the electrolysis solution at 1.0 mL H_2O_2 L^{-1} (pH = 3 and 30 mA cm^{-2} and flow = 14 L $min^{-1)}$. Insert: UV–vis of nonylphenol at treatment time (120 min) and different doses of H_2O_2: red, 0.5 mL L^{-1} ; green, 1.0 mL L^{-1} ; blue, 1.5 mL L^{-1}.

The NP's removal was verified by COD and COT (Figure 3), both analyses revealed that with higher concentrations of hydrogen peroxide there is an efficient removal of NP. Thus, at 120 min, COD indicated a removal efficiency of 90 and 92% with 1.0 and 1.5 mL L^{-1}, respectively, whereas with the lowest amount it is almost the half. A similar behavior was observed for this time in the TOC analysis.

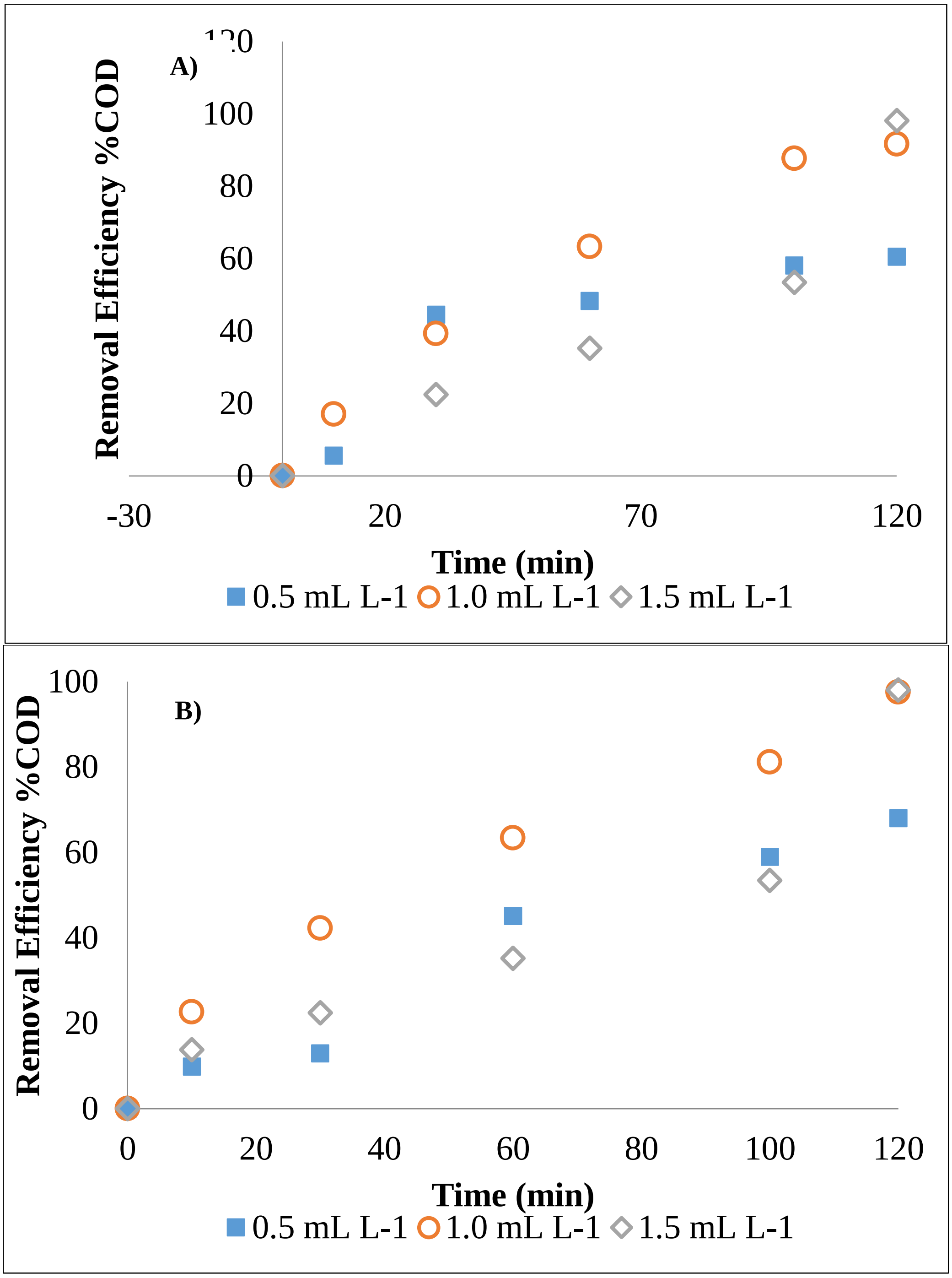

Figure 3. A) COD removal during the electrochemical treatment of NP in a continuous reactor at different H_2O_2 doses (pH = 3 and 30 mA cm^{-2} and 14 L min^{-1}) B) TOC removal during the electrochemical treatment of NP in a continuous reactor at different H_2O_2 doses (pH = 3 and 30 mA cm^{-2} and 14 L min^{-1}) (■) 0.5 mL L^{-1} (○) 1.0 mL L^{-1}, and (◊) 1.5 mL L^{-1}

The relationship between the degradation of NP and the dose of H_2O_2 is due to the production of the hydroxyl radical responsible for the degradation of the molecule, because of this ability to produce hydroxyl radicals by catalysis, either in the presence or absence of radiation, it produces 2 (•OH) per molecule of H_2O_2 [16,22]. Thus, a higher concentration of H_2O_2 in the system will induce a higher production of this radical that, together with those generated in the DDB electrode, will degrade the molecule faster. However, care must be taken with the supplied dose of H_2O_2, since a large excess can promote the formation of the perhydroxyl (•OH_2) radical, which is less reactive [23], affecting the degradation rate. Because there is no significant difference in NP removal in 2 hours of treatment when using 1.0 or 1.5 mL L^{-1} H_2O_2 (97.6 and 98%, respectively), and to avoid the production of the •OH_2 radical, 1.0 mL L^{-1} was chosen as the optimal dose.

3.2. Optimal flow in the system

The electrochemical cell was operated under different flow rates (7, 14, and 22 L min^{-1}); for each condition, the removal efficiency by means of COD (Figure 4) and COT (Figure 5) was determined.

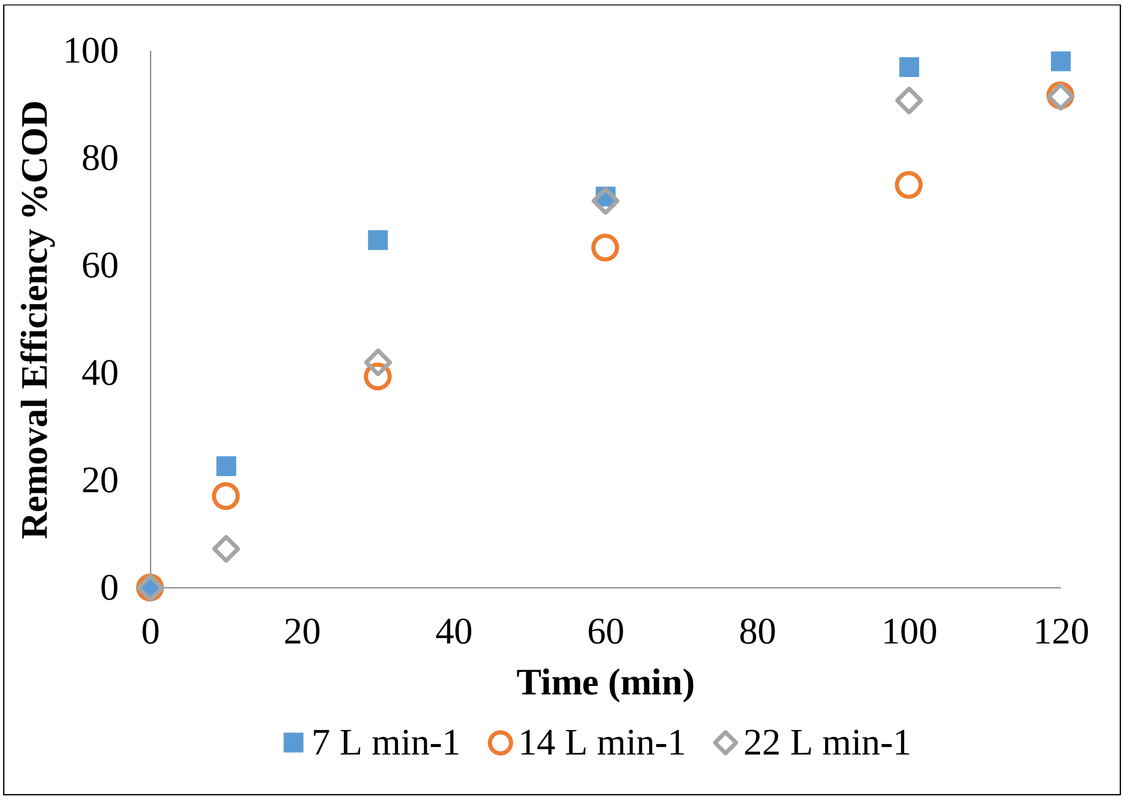

Figure 4. COD removal during the electrochemical treatment of NP in a continuous reactor at different flow rates (pH = 3 and 30 mA cm^{-2} and 1.0 mL L^{-1} H_2O_2) (◊) 22 L min^{-1}, (○) 14 L min^{-1}, and (■) 7 L min^{-1}.

After 120 min, a 98% removal efficiency was obtained with a flow rate of 7 L min^{-1}, 91.65% and 91.43% using 14 and 22 L min^{-1} at 120 min, respectively. Slow flow rate generated the highest NP removal, this is due to the fact that the solution has a longer contact time with the electrodes, facilitating the degradation by means of the physisorbed •OH radicals present in the BDD electrode surface.

TOC analysis gave similar good results, removal efficiency of 98% was observed with 7 L min^{-1}, whereas smaller values (96.14 and 85.92 %) were obtained when operating at 14 and 22 L min^{-1} after 120 min of treatment. These analyses confirm that the lower the flow in the system, the greater will be the removal of NP. These results indicate that the contact time between the contaminant and the surface of the BDD electrode increased. This point is important within the electrochemical treatment, because electrochemical reactions are heterogeneous and they can be limited by mass transfer towards the electrode. A turbulent flow behaves like a stirring inside the cell and helps to diminish the diffusion layer on the electrodes, in consequence, the contaminant reaches the electrode faster, thus improving the degradation reaction.

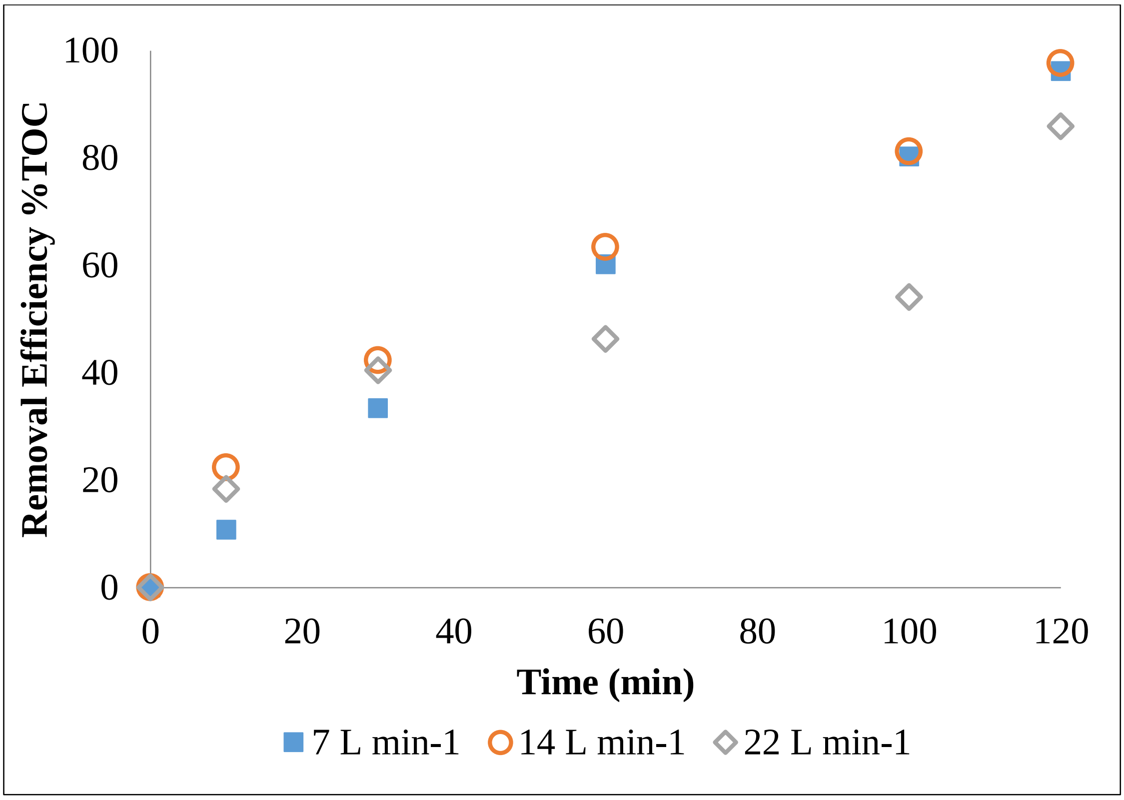

Figure 5. TOC removal efficiency during the electrochemical-H_2O_2 treatment of NP in a continuous reactor at different flow rates (pH = 3 and 30 mA cm^{-2} and 1.0 mL L^{-1} H_2O_2). (◊) 22 L min^{-1} (○) 14 L min^{-1}, and (■) 7 L min^{-1}.

Once the DDB-H_2O_2 treatment was optimized, the advantage of using the combined method instead of the pure electrochemical one [17] was confirmed (Figure 6). Both processes behaved very similar until reaching a 60-70% of TOC removal (60 min), but an optimization in the time required to achieve a removal efficiency higher than 90% was obtained with the combined method, where 120 min were required; the electrochemical treatment attained only 86% after 240 min. As the degradation of NP advances the concentration of short-chain carboxylic acids start to be very important in the solution. These compounds are very difficult to oxidize [17], therefore, the combined process permits to eliminate faster these final organic intermediates. In these conditions, a charge of 1.1 AhL^{-1} has passed through the system after 120 min of electrolysis. The current efficiency in terms of the TOC removal efficiency, using electrochemical-H_2O_2 treatment, was about 50%.

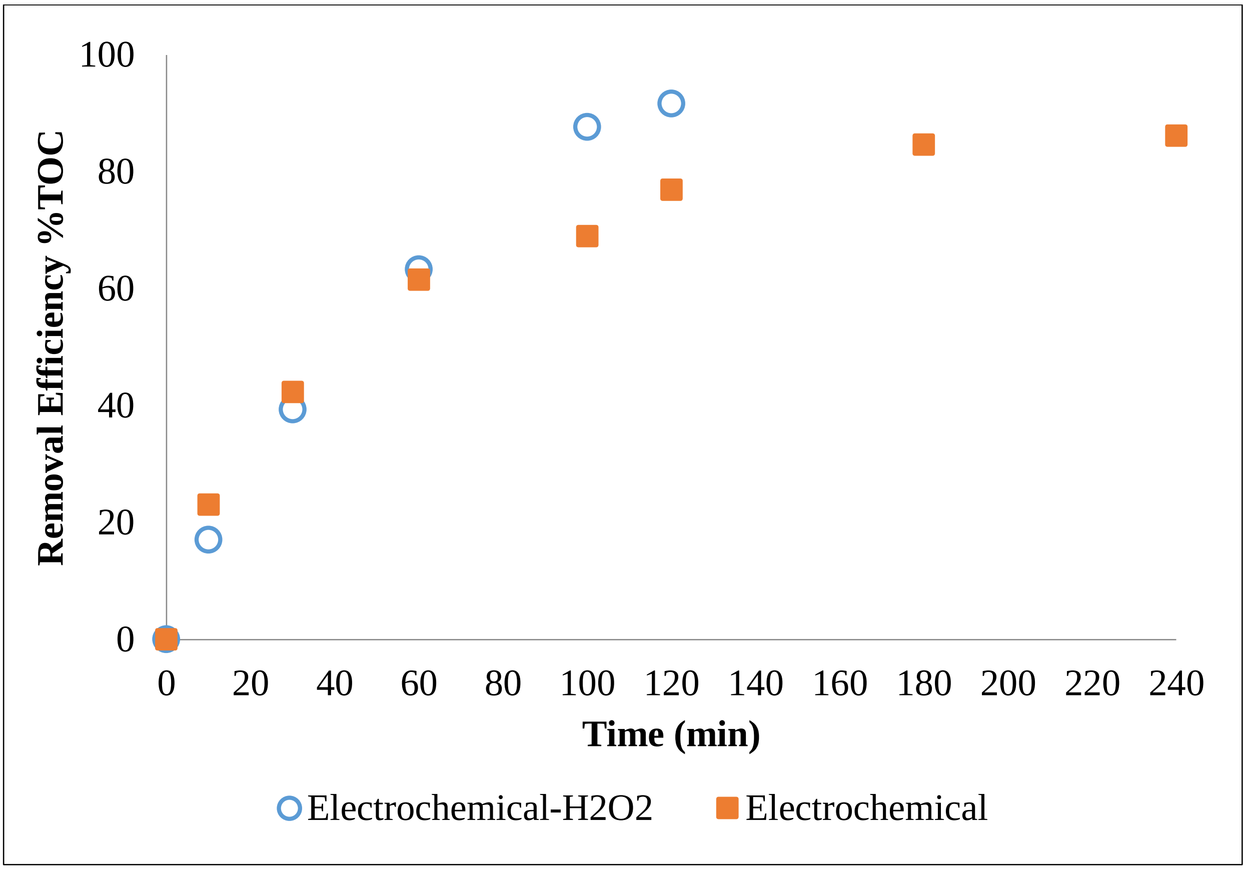

Figure 6. Comparison of TOC removal efficiency between the combined H_2O_2-electrochemical and pure electrochemical processes: (○) Electrochemical-H_2O_2 (■) Electrochemical

3.3 Energy consumption and associated cost

Table 1. Energy consumption and operational cost

[redacted]	[redacted]	[redacted]
DiaClean Reactor	0.1421	0.0053
Peristaltic pump	1.52	0.228
TOTAL	**1.662**	**0.233**

The energy consumption and operational cost for the combined electrochemical-H_2O_2 treatment are shown in Table 1. This cost is based on the charge supplied to the system and the cost of the peristaltic pump. Using equations 2 to 4, an energy consumption of 1.662 $kWhL^{-1}$ is obtained, which represents a cost of US$0.233.

Table 2 shows a comparison of the cost of treatment for NP degradation using different AOPs, where the economic viability can be deduced. The degradation with the combined H_2O_2-electrochemical BDD anode is the one with the lowest cost followed by the integrated oxidation processes O_3-electrochemical BDD anode [17]; finally, UV-O_3 [16] and the electrochemical BDD anode oxidation [17] resulted the less economically viable. The process here described represents a saving in the cost of the operation in terms of energy consumption, with excellent results for the advanced oxidation of organic compounds generated from the NP degradation, reaching a removal efficiency (COT) of 98% in only 2 hours of operation. Moreover, the addition of an aliquot of H_2O_2 during the electrochemical degradation is a very simple operation that does not represent a complication for scale-up.

Table 2. Cost of treatment in US$ per $kWhL^{-1}$ for different treatments of 4-Nonylphenol contaminated water

[redacted]	[redacted]	[redacted]	[redacted]
Electrochemical BDD anode [17]	87	240	0.4556
UV-O_3 [16]	86	120	0.2707
Electrochemical BDD anode-O_3[17]	91	120	0.2553
Electrochemical BDD anode-H_2O_2 (this work)	98	120	**0.2493**

4. CONCLUSIONS

The presence of hydrogen peroxide as oxidizing agent during electrochemical degradation induces an increase in the rate of electrochemical degradation of NP and organic compounds, when the BDD anode is used. This combined process requires less energy and attains an excellent removal of NP and the organic compounds produced during its degradation. A comparison of costs and the NP elimination efficiency with other processes indicates that the proposed process is an attractive alternative for the treatment of persistent pollutants.

References

1. Z. Mao, X.F. Zheng, Y.Q. Zhang, X.X. Tao, Y. Li, W. Wang, *Int. J. Mol. Sci*., 13 (2012) 491.
2. G.M.S. ElShafei, F.Z. Yehia, G. Eshaq, A.E. ElMetwally, *Sep. Purif. Technol.*. 178 (2017) 122.
3. S.T. Kim, Nonylphenol, *Encycl. Toxicol*., 3 (2014) 614.

4. N. Bai, R. Abuduaini, S. Wang, M. Zhang, X. Zhu, Y. Zhao, *Environ. Pollut.,* 220 (2017) 95.
5. M.C. Cheng, H.I. Chiang, J.W. Liao, C.M. Hung, M.Y. Tsai, Y.H. Chen, J.C. Ju, M.P. Cheng, K.H. Tso, Y.K. Fan, *Anim. Reprod. Sci*., 174 (2016) 114.
6. I. Shirdel, M.R. Kalbassi, *Comp. Biochem. Physiol. Part - C Toxicol. Pharmacol.,* 183–184 (2016) 28.
7. O.J. Ponzo, C. Silvia, *Toxicology*, 311 (2013) 41.
8. M. Lepretti, G. Paolella, D. Giordano, A. Marabotti, F. Gay, A. Capaldo, C. Esposito, I. Caputo, *Toxicol. Vitr.,* 29 (2015) 1436.
9. T. Raecker, B. Thiele, R.M. Boehme, K. Guenther, *Chemosphere*, 82 (2011) 1533.
10. M. Chen, R. Tang, G. Fu, B. Xu, P. Zhu, S. Qiao, X. Chen, B. Xu, Y. Qin, C. Lu, B. Hang, Y. Xia, X. Wang, *J. Hazard. Mater.*, 250–251 (2013) 115
11. B. Balakrishnan, E. Thorstensen, A. Ponnampalam, M.D. Mitchell, *Placenta*, 32 (2011) 788
12. I.R. Falconer, H.F. Chapman, M.R. Moore, G. Ranmuthugala, *Environ. Toxicol.,* 21 (2006) 181
13. G. Zheng, T. Wang, M. Niu, X. Chen, C. Liu, Y. Wang, T. Chen, *Environ. Pollut.,* 238 (2018) 783.
14. M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, H, *J. Chem. Eng.*, 284 (2016) 582.
15. E. Peralta, M. Ruíz, G. Martínez, J. Mentado-morales, L.G. Zárate, *Int. J. Electrochem. Sci.*, 13 (2018) 4625.
16. E. Felis, K. Miksch, *Water Sci. Technol,*. 71 (2015) 446.
17. C.E. Barrera-Díaz, B.A. Frontana-Uribe, M. Rodriguez-Peña, J.C. Gomez- Palma, B. Bilyeu, *Catal. Today*., 305 (2018) 108.
18. K.G. Armijos-alcocer, P.J. Espinoza-montero, B.A. Frontana-Uribe, C.E. Barrera-Díaz, M.C. Nevárez-Martínez, G.C. Fierro-Naranjo, *Water Air Soil Pollut*., 7 (2017) 228
19. G. Eisenberg, *Ind. Eng. Chem. Anal*. 15 (1943) 327.
20. S. Ellouze, M. Panizza, A. Barbucci, G. Cerisola, T. Mhiri, S.C. Elaoud, *J. Taiwan Inst. Chem. Eng.,* 59 (2016) 132.
21. V.M. García-Orozco, C.E. Barrera-Díaz, G. Roa-Morales, I. Linares-Hernández, *J. Chem.,* 2016 (2016) 1.
22. W. Song, V. Ravindran, M. Pirbazari, *Chem. Eng. Sci.*, 63 (2008) 3249.
23. T. Rodriguez, D. Botelho, E. Cleto, *Rev. Fac. Ing. Univ. Antioquia*, 46 (2008) 24.