



The use of combined treatments for reducing parabens in surface waters: Ion-exchange resin and nanofiltration

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ABSTRACT

In this study, the removal of parabens from waters, using a combined treatment of magnetic ion exchange resins and subsequent filtration through nanofiltration membranes, was investigated. The selected parabens were methylparaben, ethylparaben, propylparaben and butylparaben. Two different magnetic anionic exchanger resins, MIEX® DOC and MIEX® GOLD, and two nanofiltration membranes (NF), NF-90 and DESAL-HL, were tested. The study was carried out using mono and multicomponent systems, using deionized water and natural waters sampled from two different rivers. In this way, competitive and matrix effects could be evaluated. The results showed, that with the combined treatments, higher elimination rates were obtained. The best removal efficiencies were obtained when the DOC resin was combined with both NF-90 and DESAL-HL membranes. Thus, butylparaben and propylparaben reached removal yields around 100% with both membranes, whereas the corresponding values for methylparaben were 91%, when the NF-90 membrane was employed, or 92% when DESAL-HL membrane was utilized. The elimination rates of ethylparaben with the same treatments were 96% with the NF-90 and 97% when the DESAL-HL membrane was combined with the DOC resin. The elimination percentages were higher as the paraben alkyl chain length increased. In addition, no competitiveness or matrix effects were detected. When the MIEX® GOLD resin was used for pre-treatment, membrane fouling worsened which indicated that resin selection needs to be carefully considered to achieve the best results.

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1. Introduction

Parabens are a family of compounds that are widely used in personal care products, as food preservatives or in the pharmaceutical industry. Common paraben group members include methyl, ethyl, propyl and butylparaben. Their widespread use has resulted in their detection in human fluid samples, e.g. in human blood, urine and breast milk, of different human populations and in environmental samples, such as waste water, treatment plant effluents and in rivers (Canosa et al., 2006; Li et al., 2016). Recent reports have indicated that exposure to parabens may modulate or disrupt the endocrine system and may, therefore, have harmful consequences on human health (Okubo et al., 2001; Soni et al., 2005). The presence of emerging contaminants in the aquatic environment is widely studied. The existence of parabens in continental waters is mainly attributed to discharges from waste water plants, with methylparaben and propylparaben being the most commonly detected due to their increased use in cosmetic products (Haman et al., 2015).

The concentration range of parabens detected is variable, for example, in surface water levels between 15 and 400 ng/L have been

detected for parabens, including the sum of Benzylparaben, Butylparaben, Ethylparaben, Isobutylparaben, Methylparaben and Isopropylparaben (Brausch and Rand, 2011). Yamamoto et al. (2011) found concentrations of 670 ng/L for methylparaben, 207 for n-propylparaben and 163 ng/L for n-butylparaben in a sewerage system, and they studied their toxicity to three aquatic organisms. Toxicity increases with increasing alkyl chain length (Brausch and Rand, 2011; Yamamoto et al., 2011). Gorga et al. (2015) detected methylparaben, ethylparaben and propylparaben in the Spanish rivers Ebro, Llobregat, Júcar and Guadalquivir in maximum concentrations of 142 ng/L (Ebro River), 49 ng/L (Júcar River), 26 ng/L (Guadalquivir River). Esteban et al. (2014) detected ethylparaben, propylparaben and triclosan at maximum concentrations of 16, 38, and 184 ng/L, respectively, in the Jarama and Manzanares rivers.

As regards the removal of parabens, treatment with granular activated carbon was only effective in reducing benzylparaben, whereas treatment with ClO₂ allowed removal of >70% for methylparaben, propylparaben and benzylparaben (Gabarrón et al., 2016).

Since their introduction in the late 1950s, the use of membranes in water treatment processes has substantially increased. The development of new generation membranes and knowledge gained through research about their properties has contributed to improvements in their performance and effectiveness. There are different classifications of membranes, one of which refers to their pore size, with mi-

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Table 1List of compounds studied and physicochemical properties. ^a(Agarwala et al., 2016).

Compound	MW (g/mol)	Log Kow ^a	pKa (Scifinder Database)
Methylparaben	152.149	1.96	8.40
Ethylparaben	166.176	2.47	8.34
Propylparaben	180.203	3.04	7.91
Butylparaben	194.23	3.57	8.47

Table 2

Values of TOC, UV (254 nm), SUVA, pH and conductivity of the natural waters used as matrix.

Parameter	Verde River water	Segura River water
TOC (mg/L)	6.8	5.7
UV (254 nm)	0.097	0.116
SUVA (L/mg m)	1.4	2.0
pH	8.4	7.47
Conductivity (µS/cm)	3150	2600

Note: Total Organic Carbon (TOC); Specific ultraviolet Absorbance (SUVA).

Table 3

Properties of the membranes studied.

	NF-90	DESAL-HL
Manufacturer	Dow Chemical	GE Osmonics
Material ^a	Polyamide TF	Polyamide TF
MWCO (Da) ^a	200	150–300
J ₀ (m ³ /m ² s) ^b	2.44 10 ⁻⁶	6.48 10 ⁻⁶
Contact angle (°)	54 ^c	52 ^d
Charge (pH 7)	-24.9 ^e	-14.2 ^f

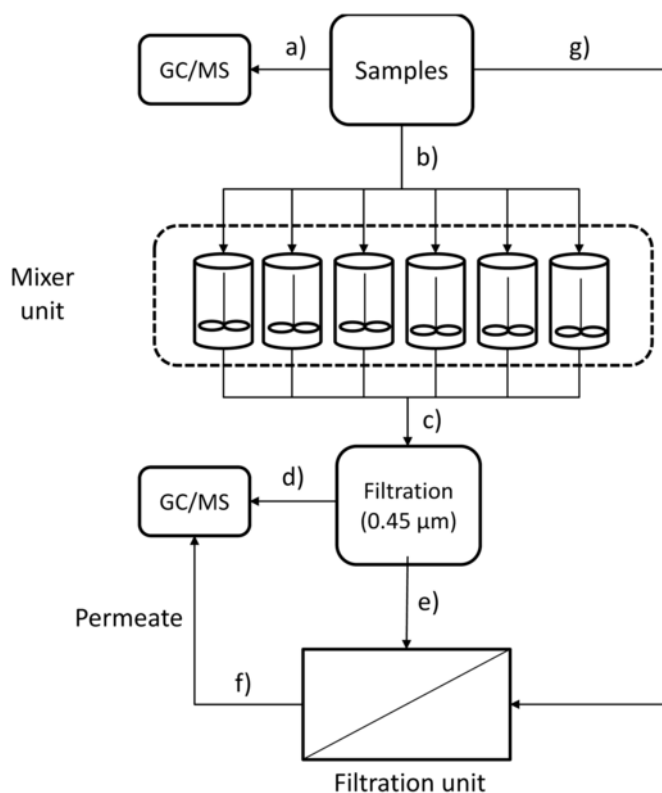
^a Information provided by the manufacturer.^b Experimentally determined value. J₀ (permeate flow with ultrapure water).^c (Boussu et al., 2006).^d (Hobbs et al., 2001).^e (Xu et al., 2006).^f (Braeken et al., 2006). MWCO (molecular weight cutoff).

crofiltration membranes, having the largest pore diameter, followed by ultrafiltration, nanofiltration (NF) and reverse osmosis membranes. Due to their pore size NF membranes are used when low weight molecules need to be separated from the solvent. In addition, because of the membrane charge, water hardness can also be partially removed (Van Der Bruggen et al., 1998). During the last decade, NF membranes have been employed to remove the colour, produced by humic and fulvic acids, in surface and groundwater (Fu et al., 1994; Tan and Sudak, 1992) and also for the removal of trihalomethane precursors and organic microcontaminants (Lin et al., 2007; Phetrak et al., 2016; Uyak et al., 2008). In addition, the use of NF is particularly interesting in cases of chronic pesticide contamination (Tepuš et al., 2009), in the reduction of by-products of chlorination (Chalatip et al., 2009), and in the treatment of emerging organic contaminants such as en-

Table 4

Quantitation, confirming ions and retention time, detections limits (LOD), quantification limits (LOQ), average recoveries and relative standard deviation (RSD) of parabens after analysis by SPE followed by derivatization and GC-MS in the SIM mode.

Parameter	Methylparaben	Ethylparaben	Propylparaben	Butylparaben
Quantitation ion	209	223	193	210
Confirming ions	193, 224	193, 238	210, 237	193, 266
Retention time (min)	6.41	6.93	7.74	8.75
LOD (ng/L)	2.6	2.7	2.5	1.8
LOQ (ng/L)	8.8	8.9	8.4	6.1
Average recovery (%)	86.8	67.9	75.2	63.7
RSD (%)	5.5	4.7	6.0	7.6

**Fig. 1.** Experimental design diagram summarizing how samples were treated; a) direct analysis, b) nanofiltration and b) and c) ion exchange plus nanofiltration.

docrine disruptors (Jin et al., 2010; Yüksel et al., 2013). For this last group of compounds different studies in which NF membranes have been employed to eliminate emerging contaminants, emphasize that removal efficiencies of contaminants are strongly affected by the physicochemical properties of the compounds (Kim et al., 2018; Bolong et al., 2009). NF has been effective in the elimination of some pharmaceutical products, obtaining percentages of reduction above 90% in some cases (Bolong et al., 2009) whereas for other structures, as Atrazine, percentages of removal were in the range of 20–85% depending on the selected NF membrane (Klöpffel and Frimmel, 2010). Yoon et al. (2006) studied the elimination of 27 endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes without including any parabens in their study. They obtained better results when they used nanofiltration membranes than when they used ultrafiltration membranes, and also noted that compounds that were more polar, less volatile and less hydrophobic were eliminated worse, indicating that these removals could be governed by hydrophobic adsorption. Bolong et al. (2009) analyzed

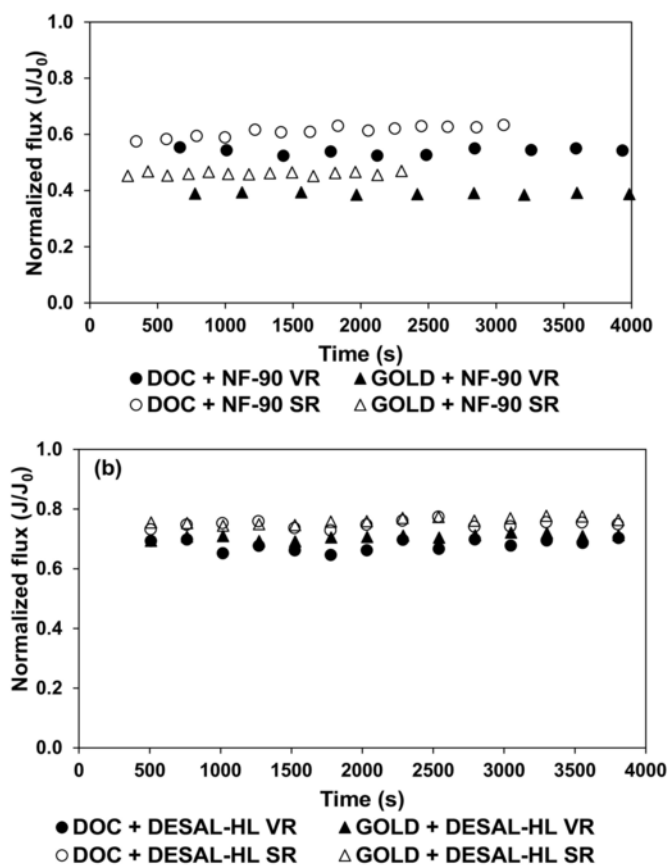


Fig. 2. Normalized flux profile versus time for each of the combined treatments was applied using the natural waters tested (Verde River (RV) and Segura (RS)) and membranes (a, NF-90 membrane; b, DESAL-HL membrane).

the use of activated carbon, oxidation, activated sludge, nanofiltration and reverse osmosis membranes, and their efficiency in the elimination of emerging contaminants present in wastewater, concluding that the mechanism of elimination of nanofiltration stands out for its great importance in the elimination of microcontaminants. Parabens were not included in this study among the pollutants studied.

However, the generalized use of NF membrane technology in the drinking water industry has been hampered by membrane fouling (Nghiem and Hawkes, 2009). Microorganisms, colloids, chemicals, and salts present in a feed solution can cause this problem. Fouling affects membrane performance by reducing solute retention. The extent and rate of membrane fouling are greatly affected by the surface characteristics of the membrane (Hong and Elimelech, 1997), the operating conditions and properties of the feed solution (Wang et al., 2008).

In recent years, studies on the use of pretreatment methods to minimize membrane fouling have been carried out; coagulation, activated carbon adsorption, advanced photooxidation, and ion exchange resin techniques have been investigated. The ion exchange processes prevent the formation of by-products and reduce the total organic carbon content of low and medium molecular weight compounds (Bourke et al., 2001). In addition, ion exchange resins can be regenerated whereas activated carbon and coagulant agents usually cannot, so this makes the use of ion exchange resins more cost effective.

There are a wide range of ion exchange resins available on the market. MIEX® resin (manufactured by Orica Chemicals) was developed in Australia in the mid-80s. Initially, its use was intended for the removal of organic matter (Aryal et al., 2015; Drikas et al., 2011), al-

though its use also improves waters quality by removing inorganic ions such as nitrate, arsenate, bromide perchlorate and chromate (Hans et al., 2016; Tang et al., 2013). The use of MIEX® resin also improves the elimination of the by-products from disinfection processes such as halogenated derivatives derived from chlorine and bromine (Bond et al., 2010). Recent studies have shown that organic compounds with high toxicity such as drugs, hormones and personal care products can also be efficiently removed by using the MIEX® resin (Lu et al., 2016). One type of substance usually found in personal care products is the group of compounds known as parabens.

As far as we know, there are no studies that address the removal of parabens from water samples with a combination treatment (i.e. ion exchange resins followed by nanofiltration). Thus, the objective of this study was to evaluate whether the combination treatment improved the removal yield of parabens when compared to the results achieved by each individual treatment. In addition, the influence of the chemical structure of the paraben on the removal efficiency will also be investigated. To carry out the study two ion exchange resins (MIEX® DOC and GOLD resin) were selected for the pretreatment stage. Two nanofiltration membranes (NF-90 and DESAL-HL membranes) were selected. The results in terms of removal efficiency and membrane fouling were evaluated using standard solutions and natural waters to which parabens had been previously added. There have not been any studies on the elimination of parabens with the resins and membranes used in this research to date.

2. Materials and methods

2.1. Reagents

Solvents (ethyl acetate and methanol), pyridine, the derivatizing reagent *N,O*-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) and 1% trimethylchlorosilane (TMCS) and milli-Q water, of chromatography grade, were acquired from Sigma-Aldrich (Steinheim, Germany). Sulfuric acid (96% w/w) and pure pharma grade sodium bicarbonate, was purchased from Panreac (Barcelona, Spain).

Four compounds were studied (Table 1): methylparaben, ethylparaben, propylparaben and butylparaben. Carbamazepine-d10, was used as an internal standard. All these substances were purchased from Sigma-Aldrich (Steinheim, Germany) and were 98–99% pure.

Oasis HLB (6 mL/60 mg) solid phase extraction cartridges used and were obtained from Waters (Milford, MA, USA).

2.2. Standard solutions

Stock solutions of parabens were prepared at 20,000 mg/L in methanol. From these stock solutions, intermediate diluted solutions of 2000 mg/L in methanol were derived. Working solutions of 50 mg/L of each compound were obtained by the appropriate dilution of the intermediate solutions in methanol. All standard solutions were stored at -20°C in amber glass bottles.

A stock solution of carbamazepine-d10 was prepared in methanol at 5000 mg/L. The working internal standard solution, with a concentration of 500 $\mu\text{g/L}$, was prepared from the stock solutions and stored at -20°C in an amber glass bottle.

2.3. Sample collection and preparation

Deionized water and two natural water samples from the Verde and Segura rivers (both located in Alicante, Spain) were used as matrices for the experiments carried out in this study (Table 2). Original paraben concentrations were determined, using the methodology described in Section 2.6, in both natural water samples. Methylparaben and ethylparaben were found at concentrations below the limits of

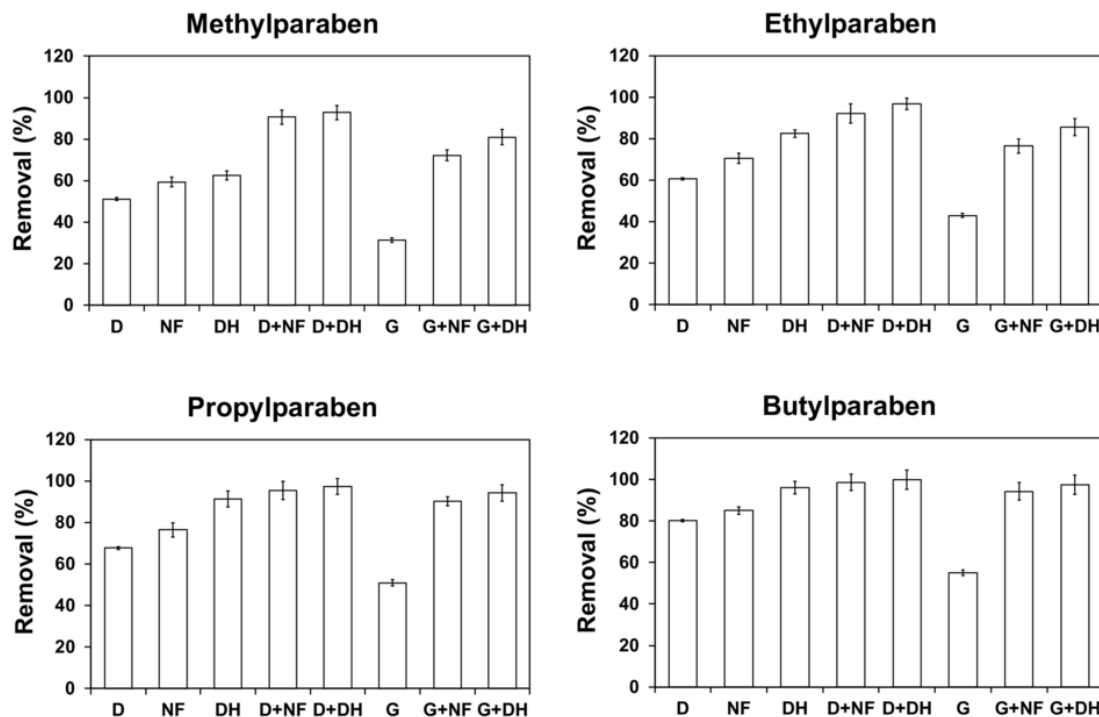


Fig. 3. Removal percentages obtained with the unique treatments (**D**, MIEX® DOC resin; **G**, MIEX® GOLD resin; **NF**, NF-90 membrane; **DH**, DESAL-HL membrane) and combined (**D+NF**, MIEX® DOC resin+NF-90 membrane; **D+DH**, MIEX® DOC resin+DESAL-HL membrane; **G+NF**, MIEX® GOLD resin+NF-90 membrane; **G+DH**, MIEX® GOLD resin+DESAL-HL membrane) for the parabens studied. Error bars indicate the standard deviation of three replicates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

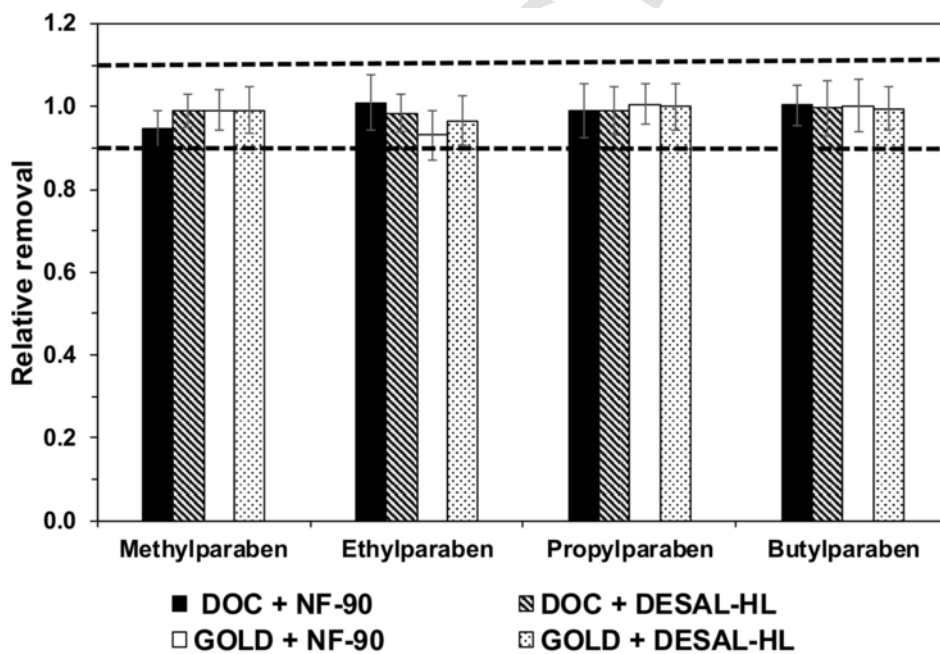


Fig. 4. Relative removal (\pm SD) of the multi-component solution, from that registered for mono-component solutions, after treatment with DOC and GOLD resins combined with NF-90 and DESAL-HL membranes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

quantification in Segura River water whereas the levels in Verde River waters were 160 and 70 ng/L respectively. For propylparaben, the concentrations were 15 and 20 ng/L in Segura River and Verde River and values below quantification level. To evaluate the removal capacity of the selected contaminants by ion exchange and NF treat-

ments, deionized water was employed with single component solutions at a concentration of 10 μ g/L for each contaminant. This matrix was also used to evaluate the existence, or not, of competitive phenomena in the removal of these substances using 10 μ g/L (of each substance) in multicomponent solutions. Afterwards, the natural wa-

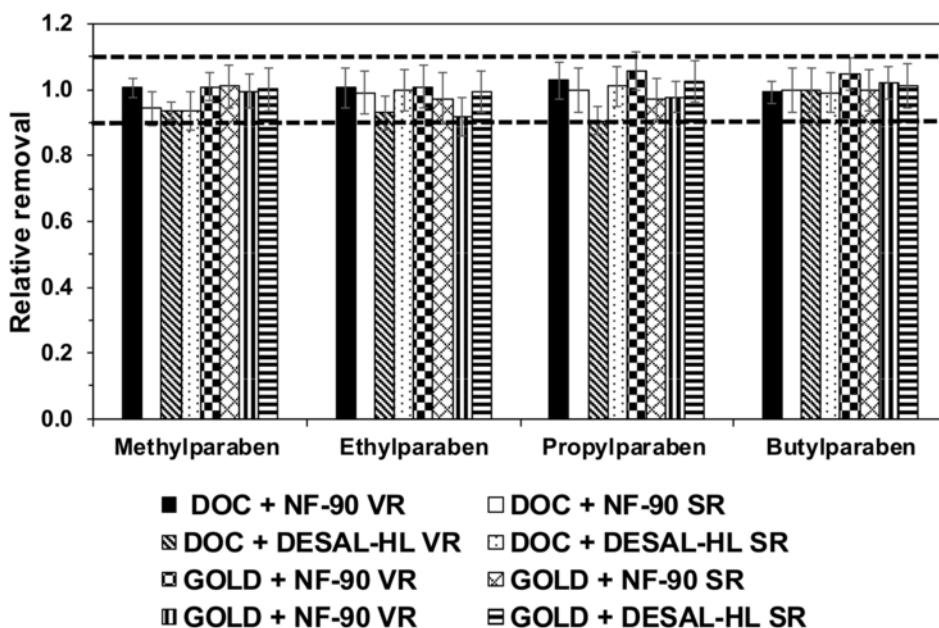


Fig. 5. Relative removal (\pm SD) of the multi-component solution prepared with water from the Verde (VR) and Segura (SR) river, compared to the one registered for multi-component solution prepared in deionized water, after treatment with DOC and GOLD resins combined with NF-90 and DESAL-HL membranes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ter samples were used to evaluate matrix influence in the adsorption and filtration processes using a multicomponent solution (again at $10\ \mu\text{g/L}$ of each compound). These surface waters were collected in 40L plastic containers that had been previously cleaned. The containers were rinsed three times with the sample waters before being eventually filled.

2.4. Magnetic ion exchange and filtration membranes

For the ion exchange tests, two strong base anion exchange resins were used. They contained a magnetic component, iron oxide, and this feature explains where the MIEX® product name comes from. The particle size of these resins is 2 to 5 times smaller than conventional resins, hence the capacity of exchange is higher, due to the increased external surface area. The two MIEX® resins studied were DOC and GOLD. The MIEX® GOLD resin presents similar characteristics to the MIEX® DOC resin, however, it has a larger surface area, larger pores and a higher capacity to remove low molecular weight material than MIEX® DOC. Resins were supplied by IXOM Watercare Inc. in slurry form in 500 mL plastic containers. Before being used, both MIEX® resins were washed three times to remove impurities and were then stored in Millipore deionized water. The optimal resin dose used was 40 mL/L and contact time 20 min for both resins.

Two nanofiltration membranes, NF-90 and DESAL-HL, were used for the filtration tests. Both membranes had a circular cross-section of 59.0 mm in diameter, with an effective surface area of $2734\ \text{mm}^2$. General information about membranes, as well as some characteristics supplied by the manufacturers, is shown in Table 3.

2.5. Equipment and experimental approach

A scheme of the experimental approach is depicted in Fig. 1. First a sample of the sample solution was taken and analyzed by GC-MS to establish the reference analyte concentration (step a). The rest of the solution was used to carry out the different treatments (steps b

and g). First, a portion of the solution was used to study the paraben removal efficiency by using the MIEX® resins (step b). To this end, a 6-position digital flocculator was used for one litre of water, containing $10\ \mu\text{g/L}$ of parabens, with 40 mL/L of each resin, at a stirring speed of 250 rpm for 20 min (the optimum dose of the resins and the contact time had been established in previous studies). The experiment was carried out at a room temperature of approximately $25\pm 0.5\ ^\circ\text{C}$. The mixture was then settled for 10 min. This solution was vacuum filtered through $0.45\ \mu\text{m}$ PVDF filters (Chmlab, Barcelona, Spain) to remove suspended particles (step c). Part of this solution was analyzed by GC-MS to evaluate the impact of resin usage (step d). With the remaining solution the combined resin and NF experiments were carried out using a NF unit with agitation (Amicon 8200, Millipore). This unit (step e) worked on loads (200 mL), with the flow direction perpendicular to the membrane surface, at a pressure of 300 kPa (maintained by nitrogen) and at a constant stirring speed of 200 rpm, to minimize the effects of concentration by polarization. Once the NF experiments had ended, the permeate was analyzed by GC-MS (step f). With these results, the efficiency of the combined treatment was evaluated (resin+nanofiltration membrane). Finally, for comparison purposes the efficiency of the NF treatment was also measured by submitting the initial sample directly to the NF unit (step g) and analyzing the permeate by GC-MS. All experiments were repeated three times.

This scheme was followed using single component solutions as well as multicomponent solutions, to check the presence of competition among the parabens. The influence of the matrix was also evaluated by comparing the results for multicomponent solutions using deionized water and actual river water samples.

Before being analyzed, all samples were acidified with 96% sulfuric acid to pH ~ 3.0 and the parabens were concentrated by means of a solid-phase extraction (SPE) procedure.

It should also be mentioned that the MIEX® resins were regenerated before each use using a solution of sodium bicarbonate (12% w/v). In addition, membranes were also renewed when the behavior for each compound had been studied.

2.6. Analytical method

Automated SPE was performed using a Dionex Autotrace 280 (Thermo Scientific) instrument. A modification of the methods described by (Gómez et al. (2007) and Hai et al. (2011) was applied for the analysis of parabens. The cartridges used were pre-conditioned with 6 mL ethyl acetate, 6 mL methanol and 6 mL Milli-Q water. The samples (500 mL each) containing the parabens were passed through the cartridges at a flow rate of 10 mL/min. The cartridges were then rinsed with 6 mL Milli-Q water and dried for 30 mins by using a stream of nitrogen. Next, the parabens were eluted from the cartridges with 4 mL ethyl acetate followed by 4 mL ethyl acetate/methanol (1:1, v/v) at a flow rate of 4 mL/min. At this point, the internal standard (100 µL of methanol solution which contained 500 µg/L carbamazepine-d10) was added to the eluates, and they were evaporated to dryness under a gentle stream of nitrogen in a heating block at 40 °C. Finally, the dry residues in the vials were derivatized by addition of 50 µL of BSTFA:TMCS (99:1) and 50 µL of pyridine, the derivatization was carried out at 60 °C for 30 mins in a heating block. The resulting solutions were cooled to room temperature and stored at 4 °C until required for analysis by GC-MS.

The analysis of the parabens was conducted using a gas chromatograph (Agilent 6890 N) (interfaced with a quadrupole mass spectrometer (Agilent 5973 N), equipped with a Gerstel cis 4+ (PTV) autosampler). An Agilent 19091S-433 HP-5MS (5% diphenyl-95% dimethylpolysiloxane) capillary column (30 m × 0.25 mm ID, df = 0.25 µm) was used. The flow rate of the carrier gas (helium) was maintained constant at 1.3 mL/min. The GC column temperature was programmed from 105 °C (initial equilibrium time 1 min) to 200 °C via a ramp of 17 °C/min and maintained for 1 min, then increased from 200 to 220 °C using a ramp of 2 °C/min and maintained for 2 mins at 220 °C. The last step was to increase the temperature up to 290 °C with a ramp of 5 °C/min, this final temperature was maintained for 1 min. The injector port and the interface temperature were maintained at 250 and 280 °C. Sample injection (1 µL) was in splitless mode. For qualitative analysis, MS full-scan mode from m/z , 50–600 was used. Apart from the mass spectrum, the relative retention times of each compound were used for confirmation of the compound. Quantitative analysis was carried out using selected ion monitoring (SIM) mode. For each compound, the most abundant and characteristic ion was selected for quantification purposes (Table 4).

Calibration standards with concentrations in the 0.5–20 µg/L range were used. The raw analyte data was normalized by taking the ratio of the compound area to the internal standard area. For the calibration, linear function R-square values higher than 0.999 were always obtained. The limits of detection (LOD) and quantification (LOQ) were experimentally estimated as the lowest concentration level able to reach a signal-to-noise ratio of 3 for LOD and 10 for LOQ (Table 4).

Accuracy –expressed as percentage recovery– and precision –expressed in terms of relative standard deviation (RSD)– were evaluated by using single component standard solutions with a concentration of 10 µg/L for each paraben. The recovery and precision values obtained are the mean of six replicates from the analysis of the standards.

Conductivity, pH, total organic carbon (TOC) and ultraviolet absorbance (UVA₂₅₄) of the Verde River water and Segura River water samples were determined from a 100 mL aliquot. The conductivity was measured using a CM 35 conductivity meter (Crison) and the pH by using a Basic 20+ pH-meter (Crison). TOC was analyzed using a Shimadzu TOC-5000 analyzer, while ultraviolet absorbance was determined using a Shimadzu UV-1601 at a wavelength of 254 nm. The reported values are the average of triplicate measurements, provided

that the relative percent difference between triplicate samples and calibration check standards was ≤5%.

3. Results and discussion

3.1. Effectiveness of the pre-treatment on nanofiltration process

Before discussing the effects of the combined treatments, it is important to note that when the NF process was the only treatment applied, the reduction in flow due to membrane fouling caused by the natural water composition was between 32% and 55% for the DESAL-HL and NF-90 membranes respectively when the Verde River water sample was used. The corresponding figures for the Segura River water sample were 25% and 46%. As can be concluded, the DESAL-HL membrane showed less fouling tendency than the NF-90 one, irrespective of the water used, which could be attributed to its smaller average pore diameter. While the fouling was more severe when the Verde River water sample was filtered, it can be justified due to the differences in water composition. Hence, the Verde River water had conductivity and organic matter content roughly 20% higher than that of the NF Segura River water. The higher flow loss when the water from the Verde River was used can be explained by concentration polarization phenomenon, which reduces the permeability of the nanofiltration membrane. Other authors have obtained a decline in the flow rate when the conductivity of the water to be filtered increases (Jarusutthirak et al., 2007; Nanda et al., 2011). It is interesting to observe that a reduction in flow was noted at the beginning of each experiment. After nanofiltration of natural waters, membrane fouling was removed with a cleaning procedure using deionized water. A 100% recovery of the initial flow was registered for both membranes, which indicated that irreversible fouling was negligible.

When the MIEX resins were incorporated to develop the combined water treatment the observed scenarios were somehow dissimilar. Fig. 2 shows plots of the normalized flux profiles (J/J_0) versus NF time for each combined treatment using the sampled natural waters: Verde River (RV) and Segura River (RS). J_0 is the permeate flow obtained when deionized water was filtered. In Fig. 2a the results achieved by the NF-90 membrane are shown while in Fig. 2b data collected for the DESAL-HL membrane are plotted. Several conclusions can be drawn.

As in the single treatment, the flow reductions occurred at the beginning of the experiment, with the flow rates remaining almost constant throughout the entire test. The largest drop in flow occurred when the NF-90 membrane was used in combination with the two resins studied and for the two natural waters evaluated. For this membrane, Fig. 2a, when the Verde River water sample was treated with the MIEX® DOC resin and was filtered, an initial drop in the flow rate of 46% was seen. While the drop in flow was 39% when the water sample from the Segura River was filtered. This improvement in the flow rate is due to the reduction of dissolved organic matter present in the water since the MIEX® DOC resin has been designed to reduce the organic matter content in drinking water (Kitis et al., 2007; Nguyen et al., 2011). These results are in accordance with the values obtained by Imbrogno et al. (2018), where they indicate that pre-treatment with MIEX® DOC resin decreases the fouling of the NF90 membrane when they work at basic pH.

When the water samples were treated with the MIEX® GOLD resin, the water from the Verde River caused a 61% drop in the flow and a 54% drop when the water from the Segura River was filtered. These results indicated that an improvement in the NF process was found when the MIEX® DOC resin was used as a pre-treatment stage while the opposite conclusion could be drawn when the MIEX® GOLD resin was introduced. In this case, although MIEX® GOLD is

also designed to reduce the organic matter content in water, the percentage of DOC reduction that it achieves is lower, especially when the water contains hydrophilic matter (Molczan and Wolska, 2016). The waters used in this work have low SUVA values which are indicative of relatively low aromaticity and hence low hydrophobicity, which in turn could decrease the effectivity of the resin treatment. Another element that could explain the reduction of the nanofiltration flow is the resin settling properties. MIEX® GOLD resin showed worse settling properties than MIEX® DOC resin in the conditions of the experiments developed, hence, fractions of resin that may remain in solution could increase the fouling of the membrane. The MIEX® GOLD resin has a more positive zeta potential than that of the MIEX® DOC which enhances the attraction to the negatively charged surface of the NF membrane. Other studies about combination treatments use of Biological activated carbon followed by MIEX® DOC before nanofiltration, reduced fouling for nanofiltration membranes to 20% when they used polyvinyl alcohol/polyamide membranes with 700 Da nominal molecular weight cut off (Aryal et al., 2015).

For the DESAL-HL membrane, Fig. 2b, when the MIEX® DOC resin was used, there was an initial drop of 32% in the flow rate for the Verde River water and 25% for the Segura River water. While the use of the MIEX® GOLD resin resulted in a 29% drop in the flow and a 24% fall for the Verde River and the Segura River waters. The incorporation of pre-treatment with MIEX® DOC resin did not reduce the fouling of the membrane with either of the two waters used. On the other hand, when treating the water with MIEX® GOLD resin, there was a certain reduction in fouling. The membrane has a lower negative surface charge and is slightly less hydrophobic than the NF-90 which may explain the results obtained.

When compared to the single NF treatment, the incorporation of the MIEX® resins can have a positive or a detrimental effect on the membrane fouling process, depending on the resin - membrane combination selected. The characteristics of the waters being treated also need to be considered, although in this study the variables which influenced the overall behaviour were not investigated. Finally, the reversibility of the fouling in the combined treatments was also confirmed in all experiments.

3.2. Study of the removal of parabens

Fig. 3 shows the results of the removal efficiencies of the parabens when the different water treatments were tested (i.e., single and combined treatments). These results were obtained using single compound solutions prepared in deionized water. For comparison purposes data of the removal efficiency attained by using only the MIEX resins is also included. It should be noted that with this treatment the lowest percentages of paraben removal were attained, with values of this parameter in the 31% to 80% range. The removal yields increased with the increased alkyl chain length of the paraben structures with the DOC resin being more effective for the removal of these substances than the GOLD one. Thus, for methylparaben, the use of the GOLD resin produced the poorest removal yield (i.e. 31%) while the best result (80%) was achieved for the butylparaben when the DOC resin was used.

When NF membranes were used as the only treatment method, paraben removal efficiencies increased, reaching values in the 60% to 96% range. Again, the best results were attained with the compounds that had longer alkyl chains. This concurs with the fact that the membrane surfaces have a certain hydrophobic character (see contact angle value in Table 3) therefore, for small substances, when the adsorption processes in the membrane surface control the removal

yield, compounds with higher hydrophobicity are more easily removed than those with lower hydrophobicity. This conclusion has been made for other compounds (Nghiem et al., 2005; Yoon et al., 2004) and, according to the reported results, can also be applied to parabens (see values of log Kow in Table 1).

When the relative behaviour of the two membranes was compared it could be concluded that the DESAL-HL membrane always achieved higher removal efficiencies than the NF-90 membrane. This improved performance is related to the different molecular weight cut off values of the membranes (Table 3).

When the combined treatment (resin and membrane) was employed the overall observation was that the combined treatments achieved, for all compounds, better removal yields than single step treatments. The resins used are strong anionic exchangers thus, in such a context, the removal efficiency for non-ionized compounds, such as the members of the parabens family, was expected to be low. However, some researchers have investigated the mechanisms of removal of non-ionized compounds (Neale et al., 2010; Tang et al., 2014). Neale et al. (2010) argued that Van der Waals and hydrogen bonding with the polyacrylate polymer of the resin were the mechanisms responsible for the removal of the non-ionized compounds through the formation of hydrogen bonds with acceptor and donor groups present in the structure. This mechanism has also been proposed for the increase of removal capacity of antibiotics by MIEX resins (Wang et al., 2016).

The removal yield achieved depends on both the compounds evaluated and the combinations of resin and membrane selected. Thus, for long chain parabens (i.e., propyl- and butylparaben) as the removal efficiencies attained using membranes were already higher than 75%, the inclusion of a pre-treatment with resins produced removal yields of 100% irrespective of the membrane used. In contrast, for parabens with shorter alkyl chains, despite the large improvement in the removal yields recorded with combined treatments, the values attained were in the 72% to 92% range for methylparaben and in the 76% to 97% range for ethylparaben, that is to say, values lower than 100%.

When the resin and membrane combinations were evaluated, the combination of the DOC resin and the DESAL-HL membrane achieved improvements in the removal of methylparaben (48% increase) and ethylparaben (17% increase). For the other two compounds, the changes recorded in the removal yields were not statistically significant. The results of the DOC and NF90 combination were similar, and although better improvements were found for propylparaben and butylparaben than when using a DESAL-HL membrane, their removal efficiency values were slightly lower.

For the GOLD resin, its combined use with the NF-90 membrane was less effective for paraben removal with improvements in the 8% to 22% range when compared to the values obtained with the treatment using only the membrane. From a statistical point of view only methylparaben and propylparaben presented significant differences with respect to the results obtained with the membrane (improvements of 22% and 18%, respectively). Likewise, the combined treatment using the GOLD resin with the DESAL-HL membrane did not provide, in general terms, improvements compared with the single treatment using just the membrane. Methylparaben proved to be an exception for which removal efficiency increased by 20%.

To summarize, the combined treatment with MIEX® resins and the DESAL-HL nanofiltration membrane achieved the best removal efficiencies for all parabens, improving the results registered in the single treatments using just the membrane or the resin. This improvement was more noticeable for parabens with shorter alkyl chain lengths.

3.3. Competitive effects on the parabens removal efficiency

Fig. 4 shows the comparison of the relative removal efficiencies obtained after the treatment of multi-component solutions, with respect to the removal percentages obtained for the mono-component solutions (i.e. relative removal value of 1).

The results showed a slight decrease, from 4% to 7%, in the efficacy of the elimination for the combined treatments under study using multicomponent solutions when compared with those achieved for single-component solutions. This variation in the efficacy of the elimination is within the error recorded in this type of test (i.e., 10%, the value indicated by dashed lines in Fig. 4). Therefore, it can be concluded that there are no competitive phenomena in the elimination of the parabens, under the conditions tested.

3.4. Influence of matrix on the parabens removal efficiency

Fig. 5 shows the relative removal (relative to that obtained with multi-component solutions prepared with deionized water) for multi-component solutions prepared with the water samples from the Verde and Segura rivers, for each of the evaluated resins- membrane combinations.

It can be concluded that the matrix of the natural waters used did not affect the capacity of the combined treatment for removing parabens from these waters, since the decrease in elimination efficiency of the compounds tested is in the 2 to 9% range, this range is within the typical error established in this type of test (as we have already indicated, 10%, dashed lines in Fig. 5).

As we have seen, the combined use of MIEX technologies and nanofiltration membranes allows us to improve the treated water quality by reducing the levels of compounds considered of environmental concern (i.e., emerging pollutants). Although the initial design of the resins is not specifically focused on the elimination of this type of substances, but rather on dissolved organic matter that has higher molecular sizes (Wang and Ni, 2013), if the samples to be treated have a low DOM content, the elimination of these contaminants can be significant, contributing to increasing the time needed for the membranes fouling, as well as acting synergistically with the membranes to reduce the presence of contaminants in the filtrate. However, the conditions under which the best results can be obtained must be carefully studied in each case.

4. Conclusions

Pre-treatment of natural waters with MIEX® resins can mitigate the process of membrane fouling due to the natural organic matter. However, a careful selection of resin is needed in order to achieve the best results, otherwise, a detrimental effect, as seen for the NF membrane, could be observed.

The combination of MIEX® resins and NF membranes improved the removal efficiencies of the shorter alkyl chain length parabens (i.e. methylparaben and ethylparaben). For propylparaben and butylparaben, an improvement was only achieved when the NF-90 membrane was used. However, the best removal efficiencies were obtained by the combined use of DOC resin with the DESAL-HL membrane.

No competitive effects were observed among the paraben compounds during their removal process. This is an interesting conclusion as, because of their widespread use, parabens are often found as contaminants in natural waters. Finally, the presence of natural organic matter did not affect the removal efficiency of the parabens. This result has important practical implications since in the event of

decreased water productivity, the quality, in term of parabens levels, is not affected.

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