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

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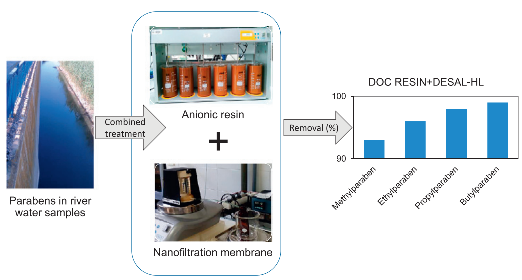
HIGHLIGHTS

- NF membrane fouling is attenuated if MIEX DOC resin is included as pretreatment.
- Combined treatments increase removal yields of shorter chain parabens.
- Removal efficiencies increase with the length of the alkyl-paraben chain.

GRAPHICAL ABSTRACT



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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.

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

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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 (Jucar 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 ClO_2 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 microfiltration 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 endocrine 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 tor other structures, as Atrazine, percentages of removal were in the range of 20–85% depending on the selected NF membrane (Klüpfel 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 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), although 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,