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Effect of magnetic ion exchange (MIEX®) on removal of emerging organic contaminants

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Abstract

In this study, the removal of nine emerging organic contaminants was investigated by using anion exchange resins. The selected compounds were carbamazepine, atrazine, simazine, estrone, bisphenol A, methylparaben, ethylparaben, propylparaben and butylparaben. Two different magnetic anionic exchanger resins were tested: MIEX® DOC and MIEX® GOLD. The optimal resin dose (40 mL/L) and contact time (20 min) had been previously determined. Once these optimum parameters were set, the effect of the initial concentration of contaminants on the removal efficiency of the contaminants by the resins was studied. The study was carried out using mono and multicomponent systems, with distilled water and natural waters, to which contaminants had been previously added, in order to evaluate the competitive and matrix effects. Results showed that the average removal percentages obtained with the MIEX® DOC

24 resin were: 51%, 61%, 68% and 80% for methyl-, ethyl-, propyl-, and butylparaben,
25 respectively. For bisphenol A the result was similar, i.e., 66%, whereas for the rest of
26 the compounds studied, removal efficiencies lower than 15% were obtained. The
27 MIEX[®] GOLD resin achieved lower elimination rates than the MIEX[®] DOC resin in all
28 cases.

29

30 **Keywords**

31 Magnetic resin; MIEX GOLD; MIEX DOC; Emerging organic contaminants.

32 1. Introduction

33 The presence of emerging contaminants in the environment has recently drawn great
34 attention among the scientific community due to their increased ubiquity and the effects
35 they have on health (Fatta et al., 2007). Substances that belong to this group include
36 pharmaceuticals, pesticides, hormones, industrial chemicals and personal care
37 products. Most of these substances are used on a daily basis by populations in large
38 quantities. As a result, these compounds are being continually introduced into the
39 aquatic environment, mainly through discharges from sewage treatment plants but also
40 through other routes, such as direct release from the skin during swimming or bathing.
41 Therefore, they are widespread in aquatic ecosystems (Ginebreda et al., 2010; Gros et
42 al., 2010), reaching concentrations in the ng/L range (Labadie and Budzinski, 2005)
43 which are close enough to their effective levels for some specific responses such as
44 estrogenic ones. Hence, these substance cause significant concern especially in
45 various water environments, including wastewater, surface water, sediments,
46 groundwater, and drinking water (Larsbo et al., 2009; Petrovic et al., 2004).

47 Due to the inherent diversity of this group of substances, their physical and chemical
48 characteristics show wide variations which, in turn, can lead to low and heterogenous
49 removal efficiencies for those compounds in common waste water treatment plants
50 (WWTPs). For example, carbamazepine, a common antiepileptic drug, is usually poorly
51 removed (~10% removal) when conventional treatments are used (Zhang et al., 2008),
52 and, therefore, ends up in surface waters (Ginebreda et al., 2010; Zhao et al., 2010).
53 Similarly, for the organonitrogen herbicides, atrazine and simazine, which are among
54 the most commonly used in the USA and Europe (De Almeida Azevedo et al., 2000),
55 removal efficiencies are typically in the range of 10-20% for atrazine and 40% for
56 simazine (Miltner et al., 1989) with conventional treatments in WWTPs. In the same
57 way, estrone, a naturally excreted steroidal hormone which can also be formed through
58 the oxidation of estradiol is another example of a substance with low removal

59 efficiencies (i.e., 53-61%) by conventional treatments in (Servos et al., 2005). As a
60 result, estrone is frequently detected in surface waters and sewage effluents at low
61 ng/L concentrations (Kolpin and Meyer, 2002). These results point out the low efficacy
62 of emerging contaminant removal that conventional water treatments processes
63 achieve for these compounds.

64 On the contrary, bisphenol A, used as an intermediate in the manufacture of epoxy,
65 polycarbonate, polysulfone and certain polyester resins (Staples et al., 1998), achieves
66 removal efficiencies in WWTPs which are higher (i.e. > 92%). Nevertheless, due to its
67 incomplete removal, it can reach the aquatic environment through various routes and
68 can contaminate surface waters and the raw water supply for drinking water treatment
69 plants (Loos et al., 2010). Finally, parabens are a group of p-hydroxybenzoic acid
70 esters with alkyl substituents ranging from methyl to butyl groups. They are often used
71 as antimicrobial preservatives in an extensive range of cosmetic, food and
72 pharmaceutical products to which the human population is exposed (Lundov et al.,
73 2009). Several studies have confirmed the presence of parabens in river water
74 (Canosa et al., 2006), and there are numerous reports available on the toxicity of
75 parabens to aquatic organisms (Dagher et al., 2012; Soni et al., 2005). Although the
76 removal efficiency in WWTPs of this family has been quoted as high (96.1-99.9%), they
77 are still considered as the major sources of parabens in the environment due to their
78 incomplete elimination (Błądzka et al., 2014).

79 For the elimination of dissolved emerging pollutants, the effectiveness of different water
80 treatment technologies has been studied. Some of them are often cited as conventional
81 technologies, which include chemical oxidation (Cai and Lin, 2016) and activated
82 carbon adsorption (Mailler et al., 2015; Sophia A. and Lima, 2018), and others are
83 quoted as advanced water treatment technologies i.e., advanced oxidation processes
84 and membrane filtration technologies. Although all options have proven effective in
85 decreasing emerging contaminant levels in treated water, each alternative has certain

86 pros and cons that should be considered. The main advantage of the advanced
87 oxidation processes is that organic contaminants are commonly oxidized to CO₂,
88 although the rate of the oxidation depends on the nature of oxidants and pollutants and
89 water conditions such as pH and temperature (Gupta et al., 2012). In addition,
90 oxidation by-products, that can be more toxic and resistant than the original
91 compounds, can be formed (Homem and Santos, 2011). Concerning the use of
92 membranes, nanofiltration membranes have shown great potential for organic
93 contaminants removal (Drewes et al., 2005), this technology does not form by-
94 products, however, the implementation of this technology has been greatly hampered
95 by membrane fouling (Taylor and Hong, 2000) and its effectiveness depends on the
96 physical-chemical properties of contaminants, solution chemistry and hydrodynamic
97 operation conditions (Bellona et al., 2004).

98 Another possibility that is currently being investigated for emerging contaminants
99 removal is the use of ion exchange resins. Ion exchange technology has been
100 traditionally employed to remove inorganic ions in water treatment systems, however,
101 the removal of organic compounds is also significant (Bolto et al., 2002). In fact, ion
102 exchange is used as a pre-treatment step prior to membrane filtration to reduce
103 membrane fouling by hydrophilic organic matter (Bäuerlein et al., 2012). This
104 technology has some limitations, pre-treatment of the water is required, if oil, grease
105 and high concentrations of organics and inorganics are present, and the management
106 of the regeneration brine (Company et al., 2007).

107 In this study, the application of the ion exchange process for organic removal using two
108 novel adsorption resins, MIEX[®] DOC and MIEX[®] GOLD is investigated. The detailed
109 description of the MIEX[®] DOC technology and its applications has been widely reported
110 (Drikas et al., 2011; Nguyen et al., 2011). The main characteristics differentiating
111 MIEX[®] GOLD resin from MIEX[®] DOC are (Gibson, Antony; Golubovic, 2015):

112 (i) rougher surface area and increased surface area that allows more molecules to
113 attach, with less steric or physical hindrance from other attached organic molecules.

114 (ii) larger pore openings: easily connecting to the surface area which allows easier
115 access to the inner bead area and its functional groups allowing increased exchange
116 capacity.

117 (iii) a unique ability to remove low molecular weight material (< 5000Da), as well as
118 high molecular weight dissolved organic carbons due to there being more room
119 between functional groups.

120 Several studies have demonstrated that pharmaceuticals and personal care products
121 including 2,4-D (Ding et al., 2012), bentazone (Liu et al., 2011), estrone (Neale et al.,
122 2010) and surfactant (Kowalska, 2008) can be removed effectively by MIEX[®] DOC
123 resin. It is worth noting that, all the studies mentioned above were conducted in mono-
124 component adsorption systems with test solutions containing one pollutant, using
125 MIEX[®] DOC resin. However, the adsorption performance (equilibrium, kinetic and
126 thermodynamic processes) of the target pollutant may have a discrepancy in mono-
127 component or multi-component systems. To our knowledge, the adsorption
128 performance and mechanism of MIEX[®] GOLD resin have not been reported for
129 emerging organics contaminants in mono-component or multi-component systems.
130 Therefore, the aim of this study is to systematically evaluate the removal characteristics
131 of carbamazepine, atrazine, simazine, estrone, bisphenol A and parabens in mono-
132 component and multi-component systems. The specific objective of the work being
133 presented, is to investigate the effects of the main operating parameters, such as
134 adsorbent dosage, contact time, concentration of contaminants and presence of
135 organic matter on the removal efficiency of carbamazepine, atrazine, simazine,
136 estrone, bisphenol A and parabens by MIEX[®] DOC and MIEX[®] GOLD resins.

137 **2. Materials and methods**

138 **2.1. Reagents**

139 Nine compounds were studied (Table 1). Atrazine, simazine, carbamazepine, estrone,
140 methylparaben, ethylparaben, propylparaben and butylparaben standards were
141 acquired from Sigma-Aldrich (Steinheim, Germany). Bisphenol A standard was
142 obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany). All standards were 98-99%
143 pure. The ChemAxon / Chemicalize server was used to calculate the pKa values for
144 the ionizable atoms of each compound, and thus determine the most prevalent charged
145 species at the different pH values (see figures in the supplementary material).

146 All solvents (acetone, acetonitrile, ethyl acetate, dichloromethane, methanol and Milli-Q
147 water), were purchased from Sigma-Aldrich (Steinheim, Germany) and were of
148 chromatography grade.

149 Pure sodium bicarbonate, pharma grade, from Panreac (Barcelona, Spain) and ortho-
150 phosphoric acid (85%) from Merck (Darmstadt, Germany) were also used.

151

152 **2.2. Sample collection**

153 Three different water samples were used in the study. Firstly, deionized water was
154 tested to evaluate the capability of MIEX[®] in lowering the levels of emerging organic
155 contaminant. Afterwards, waters from the Verde and Segura rivers (located in Alicante,
156 Spain) were used to evaluate the influence of matrix on the adsorption processes. The
157 concentration of dissolved organic carbon (DOC) and the absorbance at 254 nm
158 (UVA₂₅₄) from natural waters were determined, obtaining DOC values of 6.8 mg/L and
159 5.7 mg/L and UVA₂₅₄ values of 0.097 and 0.116 for the Verde River and Segura River
160 waters respectively. The pH and conductivity values measured for the Verde River
161 waters were 8.4 and 3150 μ S/cm, while for the Segura river waters, these values were
162 slightly lower, obtaining a pH of 7.47 and a conductivity of 2600 μ S/cm.

163

164 2.3. Sample preparation

165 Stock solutions of 2000 mg/L for carbamazepine and 5000 mg/L for bisphenol A were
166 prepared in ethyl acetate. In the case of the parabens, single compound stock solutions
167 of 20000 mg/L of each were prepared in acetone. For estrone, a 2000 mg/L stock
168 solution in methanol was prepared. The rest of the compounds were dissolved in
169 dichloromethane at a level of 5000 mg/L. Afterwards, working solutions of 50 mg/L of
170 each compound were obtained by dilution in ethyl acetate for bisphenol A,
171 carbamazepine, estrone and the parabens. Dichloromethane was used as a solvent for
172 the pesticides. All standard solutions were stored in amber glass bottles at -20 °C in a
173 freezer.

174 For the kinetic tests, solutions containing both butylparaben and atrazine at
175 concentrations of 0.5, 1.0, 1.5 and 2.0 mg/L were prepared in distilled water. These
176 solutions were used to define the optimum concentration of resin as a function of the
177 concentration of selected contaminants.

178 Finally, for each compound, a single component solution of 2 mg/L in distilled water
179 was prepared. In addition, combined solutions of all compounds at the same
180 concentration level (i.e. 2 mg/L) were also prepared in distilled water, in Verde river
181 water and in Segura river water. These diluted solutions were used to carry out the
182 adsorption experiments in mono-component and multi-component systems (to evaluate
183 the existence of competitive and matrix effects).

184

185 2.4. Magnetic Ion Exchange

186 Two kinds of Magnetic Ion Exchange resins namely MIEX[®] DOC and MIEX[®] GOLD
187 were used in this study. The resins were supplied by IXOM Watercare Inc.-formerly

188 Orica Chemicals- (Melbourne, Australia) in slurry form in 500 mL plastic containers.
189 The containers were filled with approximately 90% resin and 10% carrier water by
190 volume. Before being used, both MIEX[®] resins were washed three times to remove
191 impurities and stored in Millipore deionized water.

192

193 **2.5. Batch adsorption experiments**

194 Adsorption experiments on emerging organic contaminants in MIEX[®] resins were
195 carried out using the batch approach. Batch experiments were conducted in jar tests
196 using 1000 mL glass beakers at a room temperature of 25 ± 0.5 °C.

197 In the first part of the study, kinetic tests were conducted. The objective of such tests
198 was to determine the effects of resin concentration and contact time on the removal of
199 two compounds, butylparaben and atrazine. This was a two-stage study. In the first
200 stage, the required MIEX[®] resin concentrations were defined for different
201 concentrations of butylparaben and atrazine (0.5, 1.0, 1.5, 2.0 mg/L). Resin doses of 4,
202 10, 25, 40, 55, 70 and 90 mL/L were tested. Glass beakers were filled up with 1000 mL
203 of unfiltered test water, placed on the jar tester and dosed with the appropriate
204 amounts of resin. Afterwards, the content of the jar was mixed at 250 rpm for 20 min at
205 room temperature and then, it was allowed to settle for 10 mins. A supernatant water
206 sample was taken and filtered using 0.45 µm PVDF syringe filters (Chmlab, Barcelona,
207 Spain) before being analysed by HPLC. All measurements were conducted in triplicate,
208 and the jar tests were conducted in parallel.

209 In the second stage, contact times between resins and contaminants were established.

210 An optimum resin dose was chosen based on dose-response experiments. One litre of
211 the water being tested was placed in a glass beaker, dosed with the appropriate
212 amount of resin, and mixed at room temperature at a stirring rate of 250 rpm on a jar
213 test apparatus. Meanwhile, aliquots of 1 mL were carefully extracted with a syringe in

214 the mid depth of the beaker at predefined contact times of 5, 10, 20, 30, 40, 50 and 60
215 mins. During the test, the total volume of the extracted aliquots did not change the
216 concentration of the resin. All extracted samples contained (approximately) equal
217 quantities of resin; they were immediately filtered through 0.45 µm PVDF syringe filters
218 and analyzed by HPLC.

219 Based on the results obtained in these two previous stages the optimal MIEX[®] dose
220 and mixing time were established.

221 In the second part of the study, the effectiveness of the MIEX[®] resins in removing the
222 rest of the selected compounds was evaluated. To each glass beaker, the selected
223 MIEX[®] resin dose was added and 1000 mL of an aqueous pollutant solution at 2 mg/L
224 concentration (individually and combined). The MIEX[®] adsorption experiments were
225 carried out according to the procedure described previously. The pH of the solutions
226 was not monitored during the experiments, however, a pH measurement was
227 performed at the beginning of the experiment and another at the end. At the end of the
228 experiment, the treated water was immediately filtered through 0.45 µm PVDF syringe
229 filters. Samples were stored in amber glass vials in a refrigerator at 4 °C until required
230 for analysis. Samples were also analyzed before the adsorption experiment. The
231 emerging contaminants removal yield was calculated for each run using the following
232 expression

$$233 \quad \% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100$$

234 where C_i and C_f are the initial and final concentration (in mg/L) of the contaminants in
235 the samples. All the experiments were carried out in triplicate and the average values
236 were reported.

237 The MIEX[®] resins were regenerated before each use using a solution of sodium
238 bicarbonate (12% w/v). MIEX[®] (100 mL) was mixed (at 250 rpm) with the sodium
239 bicarbonate aqueous solution (900 mL) for 30 mins and allowed to settle for 10 mins.

240 Afterwards, the sodium bicarbonate solution was decanted and distilled water (900 mL)
241 was added to the MIEX[®] resin. The mixture was stirred for 30 mins. After settling for 10
242 extra mins the wash water was decanted. This rinse method with distilled water was
243 repeated three times.

244

245 **2.6. Instrumental analysis**

246 After the adsorption experiments, the concentrations of the selected pollutants were
247 determined by High Performance Liquid Chromatography (HPLC) using a liquid
248 chromatograph Agilent 1100 equipped with a UV detector. The stationary phase was
249 an Ascentis RP-Amide 5 μm of 150 mm x 4.6 mm (Sigma-Aldrich, Steinheim,
250 Germany) equipped with a pre-column Ascentis RP-Amide 5 μm of 20 mm x 4.0 mm
251 (Sigma-Aldrich). Samples (20 μL) were manually injected into the mobile phase, which
252 consisted of a mixture of acetonitrile/ultrapure water (0.1% H_3PO_4) (55:45, v/v), at a
253 flow rate of 1.0 mL/min. The detection wavelength was fixed at 220nm for atrazine,
254 simazine, carbamazepine and estrone; 254nm for the parabens and 278nm for
255 bisphenol A.

256 Peak identification was performed by comparison with retention times of standard
257 solutions.

258 The linearity of the calibration curves was verified by triplicate analysis of standard
259 solutions containing 0.05, 0.1, 0.3, 0.5, 1.0, 3.0 and 5.0 mg/L for atrazine, simazine,
260 carbamazepine, estrone and parabens. Table 1 shows the coefficient of determination
261 (r^2) and limits of detection (LOD) and quantification (LOQ) for each compound. Linearity
262 was checked by means of the lack of fit test in all cases through the manuscript.

263

264 **2.7. Other analytical methods**

265 Conductivity, pH, dissolved organic carbon (DOC) and ultraviolet absorbance (UVA_{254})
266 of the Verde river water and Segura river water samples were determined from a
267 100mL aliquot. DOC was analyzed using a Shimadzu TOC-5000 analyzer, while pH
268 was measured using a Basic 20+ (Crison) pH-meter and the conductivity was tested
269 using a CM35 (Crison) conductivity meter. Ultraviolet absorbance was determined
270 using a 1 cm quartz cell on a Shimadzu UV-1601 spectrophotometer.

271 In all cases, the reported values are the average of triplicate measurements, provided
272 that the relative percent difference between triplicate samples and calibration check
273 standards was $\leq 5\%$.

274

275 **3. Results**

276 **3.1. Effect of adsorbent dose at different analyte concentrations**

277 In order to establish the optimum resin dosage, four kinetic assays were carried out. In
278 two of these assays the MIEX[®] DOC resin was employed while in the others the MIEX[®]
279 GOLD resin was used. In these assays, different concentrations of butylparaben and
280 atrazine were tested. The resin concentrations ranged from 4 mL/L to 90 mL/L. The
281 mixtures (analyte and resin) were continuously stirred at 250 rpm during the duration of
282 the experiments, i.e. 20 minutes (Humbert et al., 2008; Zhang et al., 2006).

283

284 **3.1.1. MIEX[®] DOC resin**

285 Fig. 1 and Fig.2 show the effect of the MIEX[®] DOC resin dosage on butylparaben and
286 atrazine removal efficiency respectively. The concentrations ranged from 0.5 to 2 mg/L.
287 From these results, it could be concluded that no differences were found in the removal
288 efficiency irrespective of the concentration of the analyte employed. However,
289 differences arose when the results at different resin dosages were compared. As can

290 be seen in Fig. 1, the removal efficiency of butylparaben depends on the dose of resin
291 used, with the efficacies being higher as the dose is increased. However, the
292 relationship is little linear. Hence, at high resin dosage, the removal efficiencies of
293 butylparaben were higher than 80%. Nevertheless, at lower resin dosages (i.e. 4 mL/L)
294 the removal efficiencies were lower than 50%. It is interesting to note that changes in
295 the removal efficiencies were more noticeable at lower than at higher resin
296 concentration levels. Hence a 6-fold increase in the resin concentration (i.e. from 4 to
297 24 mL/L) induced a 1.7-fold increase in the removal efficiency (from 45 to 80%).
298 However, a 10-fold increase (from 4 to 40 mL/L) of the resin level improved the
299 removal of butylparaben by a factor of 2.

300 Regards the atrazine, (Fig. 2) lower removal efficiencies were obtained than for
301 butylparaben. The removal efficiencies of this substance also varied according to the
302 dosage of resin used, however, in this case, the dependence showed a linear tendency
303 with the dosage of resin used from 10 mL/L. Using resin dosage levels lower than 24
304 mL/L produced removal efficiencies lower than 5%. These results slightly improved up
305 to a maximum of 15% when the resin concentration increased up to 85 mL/L. The
306 analysis of the data established, within a 95% probability, demonstrated that the
307 relationship between the removal efficiencies and the dosage of resin used was linear,
308 with a mean correlation coefficient, i.e, the average correlation coefficient for all
309 selected concentrations, of 0.9987.

310 With these results a resin dose of 40 mL/L was considered a good compromise
311 solution between removal efficiency for both compounds evaluated and amount of resin
312 needed. This value is within the concentration range used by Aryal et al., (2015) for the
313 pretreatment of secondary sewage effluents (i.e. 16 - 64 mL/L) (Aryal et al., 2015). A
314 higher dose would increase the removal efficiency for atrazine but only slightly for
315 butylparaben and would also imply a higher process cost.

316 **3.1.2. MIEX® GOLD resin**

317 Fig. 1 and Fig. 2 show the effect of the MIEX[®] GOLD resin dosage on butylparaben
318 and atrazine removal efficiency. Again, different analyte concentration levels were
319 tested (i.e. from 0.5 to 2 mg/L). As can be concluded the contaminant removal
320 efficiency did not change when its concentration increased.

321 Concerning the elimination of butylparaben (Fig. 1) it can be observed that at 4 mL/L
322 resin dosage level the removal yield was roughly 25%. An increase of the resin
323 concentration to 24 mL/L doubled the removal efficiency, however further increases in
324 resin level only improved the removal up to a maximum of 76%.

325 Regarding the removal of atrazine (Fig. 2), lower yields than for butylparaben were
326 achieved. For this compound, the removal efficiency ranged from 2% (at 5 mL/L) resin
327 concentration up to 12% (at 90 mL/L). The atrazine removal efficiency showed a linear
328 dependence with the resin concentration for values higher than 10mL/L, with a
329 correlation coefficient of 0.9983.

330 As in the previous section, 40 mL/L was considered a good compromise resin dose for
331 both compounds. Although a higher dose would imply higher removal yields for
332 atrazine, the increase on the butylparaben removal efficiency would be marginal at
333 higher resin doses (i.e. lower than 5 % of the achieved value at 40 mL/L) with an
334 increase in the operating costs. In addition, the selection of this value allowed a direct
335 comparison between the two used resins at the same dose.

336

337 **3.2. MIEX[®] DOC resin Vs MIEX[®] GOLD resin**

338 When the behavior of the two resins was compared, we can observe that the MIEX[®]
339 DOC resin provided higher removal efficiencies than those achieved by the MIEX[®]
340 GOLD with an observed improvement of about 25% and 2% for butylparaben and
341 atrazine respectively, when studies were carried out at a dose of resin of 40mL/L.
342 Although the improvement for atrazine was small, after performing a test it could be

343 concluded that, with a 95% probability level, the slope value of % removal vs resin
344 dose for the MIEX[®] GOLD resin was statistically lower than that reported for the MIEX[®]
345 DOC resin (0.085 versus 0.111), indicating that, statistically speaking, the MIEX[®] DOC
346 resin was, in the conditions used in this study, more effective in the removal this
347 compound.

348 It was also observed that at resin doses lower than 40-50mL/L the differences are more
349 significant than at higher resin doses for experiments with butylparaben. For example,
350 for a resin dose of 25mL/L the MIEX[®] DOC resin removed 22% more butylparaben
351 than the MIEX[®] GOLD resin. On the other hand, for a resin concentration around
352 70mL/L MIEX[®] DOC resin achieved a 15% higher removal than the MIEX[®] GOLD
353 resin.

354 This result is in line with the work recently published by Mołczan and Wolska, (2016)
355 where they indicated that MIEX[®] DOC resin has a slightly higher capacity to remove
356 dissolved organic carbon than MIEX[®] GOLD resin for a dosage of 10 mL/L, when they
357 treated natural waters with slightly hydrophilic organic matter character. They also
358 found that at high resin doses the differences between the two resins decreased and
359 that the MIEX[®] GOLD resin achieved a larger reduction in the content of the organic
360 matter responsible for the formation of trihalomethanes due to its greater affinity for
361 hydrophobic compounds.

362

363 **3.3. Effect of contact time**

364 An experiment to ascertain the optimum contact time was conducted. To this end, four
365 additional assays were carried out, two for each resin. Butylparaben and atrazine were
366 used at a concentration level of 2 mg/L. The results are summarized in Fig. 3.

367 As can be seen, the behavior of the two resins was qualitatively similar. The removal
368 efficiency increased with contact time up to 10 minutes. Above this time the maximum

369 removal yield was achieved. This trend was noted irrespective of the compounds
370 monitored. Thus, an optimum contact time of 20 minutes was selected to ensure that
371 equilibrium was achieved. This time coincides with that documented and used by other
372 authors (Humbert et al., 2008; Zhang et al., 2007).

373

374 **3.4. Emerging organic contaminants removal by ion exchange**

375 Tests of emerging organic pollutants removal were carried out using solutions of 2
376 mg/L of each compound in distilled water. First, the removal of each compound was
377 tested individually, afterwards, the removal efficiency was monitored for a
378 multicomponent solution to investigate the existence of competitive removal effects.
379 Finally, water from the Verde River and Segura River were used (in multicomponent
380 solutions) to assess whether the presence of the matrix modifies the removal
381 efficiency. In these assays, the optimum resin dosage level and contact time used were
382 as previously described (i.e. 40 mL/L and 20 mins).

383

384 **3.4.1. Mono-component tests**

385 Results for solutions containing just one of the selected substances are presented in
386 Fig. 4. As can be seen, removal efficiencies varied from one emerging contaminant to
387 another irrespective of the resin employed. Atrazine, being the compound that
388 achieved the lowest removal efficiency (8% and 6%) and Butylparaben being the most
389 efficiently removed (80% and 55% respectively). The trend was similar for the two
390 resins tested although, as has been already presented above, the MIEX[®] DOC resin
391 always obtained better results than the MIEX[®] GOLD one.

392 Regarding the comparison of the results recorded for each compound, it should be
393 noted than for parabens the removal efficiency increased as the length of the alkyl

394 chain length of the ester functional group of the hydroxybenzoic acid increased. This
395 change in structure influences the hydrophobic character of the compound, as can be
396 also observed in Fig. 4 through the change in LogKow values. All these compounds are
397 acidic, and at the pH value of their solutions (i.e. pH values between 5.8 and 7.5), the
398 structure is mainly non-ionized based on their respective pKa values (Table 1)
399 (Agarwala et al., 2016).

400 The resins used are strong anionic exchangers thus, in such a context, the removal
401 efficiency for non-ionized compounds was expected to be low. However, some
402 researchers have investigated the mechanisms of removal of non-ionized compounds
403 (Neale et al., 2010; Tang et al., 2014). Neale et al., (2010) argued that Van der Waals
404 and hydrogen bonding with the polyacrylate polymer of the resin were the mechanisms
405 responsible for the removal of the non-ionized compounds used in his study. In line
406 with this, parabens are compounds with both hydrogen acceptor and donor groups
407 which could intervene in the formation of hydrogen bonds. The donor atom could
408 contribute to the removal of these type of substances by processes in which the non-
409 ionized fraction of the compound would be involved. This process would produce the
410 formation of hydrogen bonds with the O or N atoms of the amide group of the polymer
411 of the resin. The acceptor atoms of these structures could, in turn, interact with the
412 hydrogen bonded to the nitrogen of the amide group, although the lower strength of this
413 hydrogen bridge (due to the lower electronegativity of the nitrogen) as well as steric
414 impediments, would favour the first possibility. Therefore, in the process of removal of
415 these substances both phenomena could be involved. Ion exchange for the ionized
416 fraction of the substances (3%) and bonds by hydrogen bridges through the hydroxyl
417 group by interaction with the oxygen of the amide group of the polymer of the resin for
418 the non-ionized fraction (97%).

419 A similar scenario could be stated for bisphenol A although, in this case, the lower
420 ionized fraction of the compound at the pH values at which the presented research was

421 performed, suggests that the interaction through hydrogen bonds would have a higher
422 impact in the mechanism causing the removal of this substance. In this case, this
423 structure has two hydrogen donor atoms and two acceptors although, again, the option
424 of intervening as a donor of hydrogen atoms seems the most feasible.

425 In contrast, atrazine and simazine have lower elimination efficiencies irrespective of the
426 resin employed in the experiment, despite having log Kow values similar to those of the
427 parabens and bisphenol A. These amines have structures with several protons with
428 different acidity which means that in solution there exists a diverse medium with
429 variable net charge ranging from +1 to -1 (Fig. 5). At pH values between 6 and 7, the
430 calculated net charge is slightly positive (Fig. 5), due to the presence of species E, H
431 and I (structures of each species are shown in Table S.1 in the supplementary
432 material). This situation would cause elimination by an ion exchange mechanism to be
433 less likely for these substances. Moreover, although both amines have both hydrogen
434 donor and acceptor groups the interaction with the resin polymer would be weaker than
435 previously indicated for parabens and bisphenol A, since nitrogen atoms will always be
436 involved. Another consideration is the possible existence of steric impediments as a
437 consequence of the participation in the bonds of secondary amine groups. All these
438 phenomena could possibly explain the low elimination values recorded for these
439 substances. Further research is needed to clarify the actual mechanism responsible for
440 this experimental data.

441 Carbamazepine and estrone are two substances whose acid-base characteristics
442 indicate that they are in a neutral form at the pH value at which the study was carried
443 out. Therefore, the possibility of elimination via ion exchange can be excluded in
444 advance, reducing the effectiveness of their elimination by the resins. As for its ability
445 to form hydrogen bonds, carbamazepine has a single donor atom (the terminal
446 nitrogen) and an acceptor atom (that of the contiguous carbonyl group). This
447 conformation may seem ideal for forming a double hydrogen bond having the structure

448 as the resin (as occurs in peptides and chains in genetic material), however, as the low
449 elimination efficiencies indicate, other factors are preventing these compounds from
450 being removed from the solution. Steric hindrance could be responsible as estrone is
451 the structure that possesses the greatest volume. Thus, the Van der Waals volume for
452 this substance is 263.3 \AA^3 compared to 221.4 \AA^3 for the next compound in order,
453 bisphenol A, and 135.7 \AA^3 for the compound of the series with the smallest volume,
454 methylparaben.

455 These results demonstrate the complexity of the phenomena involved in the elimination
456 of each compound and the influence of contaminant characteristics on removal
457 efficiency.

458

459 **3.4.2 Multi-component tests. Competitive effect**

460 The first two columns in Fig. 6 show the comparison of the relative removal efficiencies
461 (\pm SD) obtained after the treatment with MIEX® DOC and MIEX® GOLD resins of multi-
462 component solutions in distilled water (DI). Data are referred to results obtained with
463 single component solutions.

464 Although the results show a slight decrease in elimination efficiency for the compounds
465 tested, that is, mean relative elimination values less than one, this variation is not
466 significant when within the margin of error that is obtained with this type of test (i. e.
467 10%, the value indicated by the dashed lines in the figure). Therefore, the results
468 obtained indicate that there is no appreciable competitive effect on the elimination of
469 these pollutants.

470

471 **3.4.3. Multi-component tests. Effect of matrix**

472 To test the influence of the matrix on the removal efficiencies of the selected
473 compounds, two natural water, Verde River and Segura River, water samples were
474 used to carry out multicomponent removal tests, the obtained results are shown in Fig
475 6.

476 As can be seen in Fig. 6, for both matrices, the percentage of elimination of the
477 compounds studied is not strongly affected by the matrix used, since they fall within or
478 close to the margin of error (indicated by the dashed lines in Fig. 6). A closer look at
479 this graph reveals that the Verde river water matrix produced a slight decrease in the
480 removal efficiency of the contaminants when MIEX® DOC resin was tested. For the
481 Segura River water this reduction did not take place. It is interesting to note that the
482 Verde River water had a total organic matter content and conductivity 20% higher than
483 that of the Segura river water, hence competition among the ions (mainly chlorides and
484 sulfates) or the organic matter present in natural waters and the studied contaminants,
485 can lead to a reduction in the removal of the latter.

486 As regards the organic matter content, the values of DOC in natural waters indicate
487 that the natural waters used had a low content of total organic matter with TOC levels
488 of 6.78 and 5.70 mg/L for Verde river and Segura river water samples. In addition, the
489 specific ultraviolet absorbance (SUVA) was determined as the UVA/ DOC ratio (L/mg
490 m). The SUVA values calculated for the Verde and Segura rivers water samples were
491 1.4 L/mg m and 2.0 L/mg m respectively. Regarding the characteristics of the organic
492 matter, according to Teixeira and Rosa, (2003), for SUVA values lower than 3 L/mg m ,
493 dissolved organic carbon is composed mainly of non-humic materials, hence organic
494 matter can be classified as relatively hydrophilic, and with small molecular weights,
495 which could decrease the removal yields. The fact that the selected natural waters had
496 low concentrations of organic matter and that anions, which are found at higher
497 concentrations, have a strong affinity for anionic exchange resins makes the effect of

498 competitiveness that may have the organic matter low. Hence the influence of the
499 anions content of water is a more feasible explanation for these results.

500

501 **4. Conclusions**

502 The removal of several emerging organic contaminants by MIEX[®] resins has been
503 investigated. The optimal conditions were found to be, a resin dosage of 40 mL/L and
504 20 minutes contact time. Removal efficiencies varied depending on the nature of the
505 compounds, being higher for members of the paraben family and bisphenol A than for
506 the other four compounds evaluated: atrazine, carbamazepine, simazine and estrone.
507 The DOC resin always provided higher removal efficiencies than the GOLD resin,
508 irrespective of the compounds evaluated. The mechanisms involved in the removal
509 seemed to be dependent on the chemical properties of the contaminants which explain
510 the variability in the results encountered and the differences regarding the role of the
511 resin. No competitive effects among the contaminants were detected when
512 multicomponent solutions were employed, and no effects of other components present
513 in natural water from rivers on the removal yield were noticed which is important from a
514 practical point of view. Because of their wide usage, emerging contaminants are found
515 as mixtures of compounds and are often detected in natural waters. The results of this
516 work highlight that further research is needed in order to completely understand the
517 interaction of organic compounds with the ion exchange resins.

518

519

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525

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Figure Captions

694 **Fig. 1.** Effect of resin MIEX® DOC and MIEX® GOLD dosage on removal efficiency in
695 the concentration range from 0.5 to 2 mg/L for Butylparaben.

696 **Fig. 2.** Effect of resin MIEX® DOC and MIEX® GOLD dosage on removal efficiency in
697 the concentration range from 0.5 to 2 mg/L for Atrazine.

698 **Fig. 3.** Effect of contact time for butylparaben (BP) and atrazine (A) removal using resin
699 dosage level of 40 mL/L using both resins (DOC and GOLD).

700 **Fig. 4.** Removal percentages obtained with the MIEX® DOC and MIEX® GOLD resins
701 for the nine contaminants studied.

702 **Fig. 5.** Distribution of species and net charge of atrazine as a function of the pH of the
703 solution.

704 **Fig. 6.** Relative removal efficiency (\pm SD) obtained for a multi-component solution after
705 treatment with MIEX® DOC and MIEX® GOLD resins. The multi-component solution
706 were prepared with Distilled Water (DI), water from the Verde River (VR) and water
707 from the Segura (SR) River.

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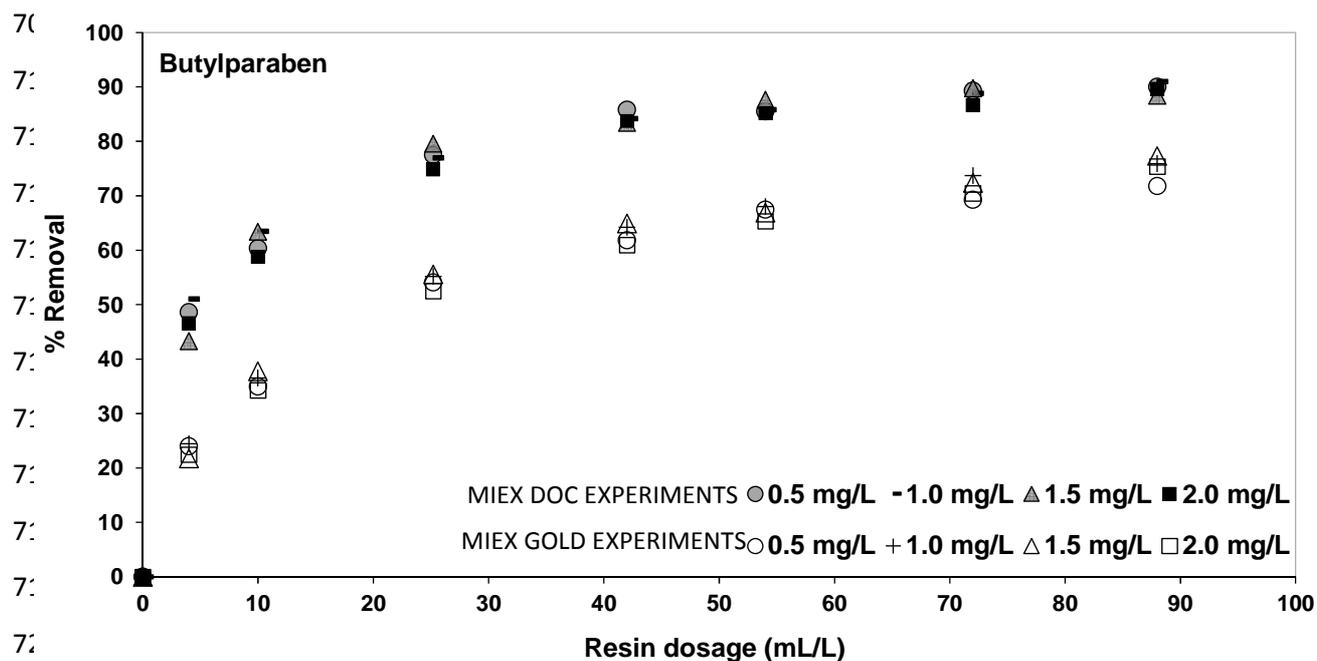


Fig.1. Effect of resin MIEX[®] DOC and MIEX[®] GOLD dosage on removal efficiency in the concentration range from 0.5 to 2 mg/L for Butylparaben.

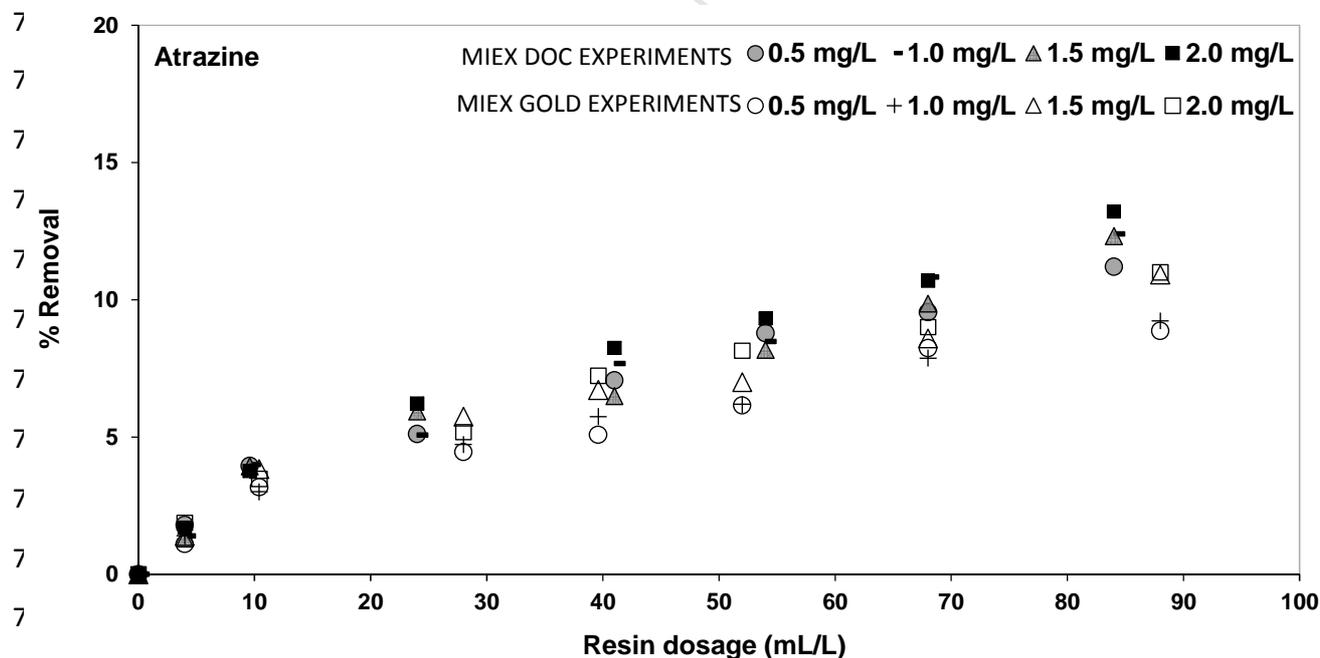
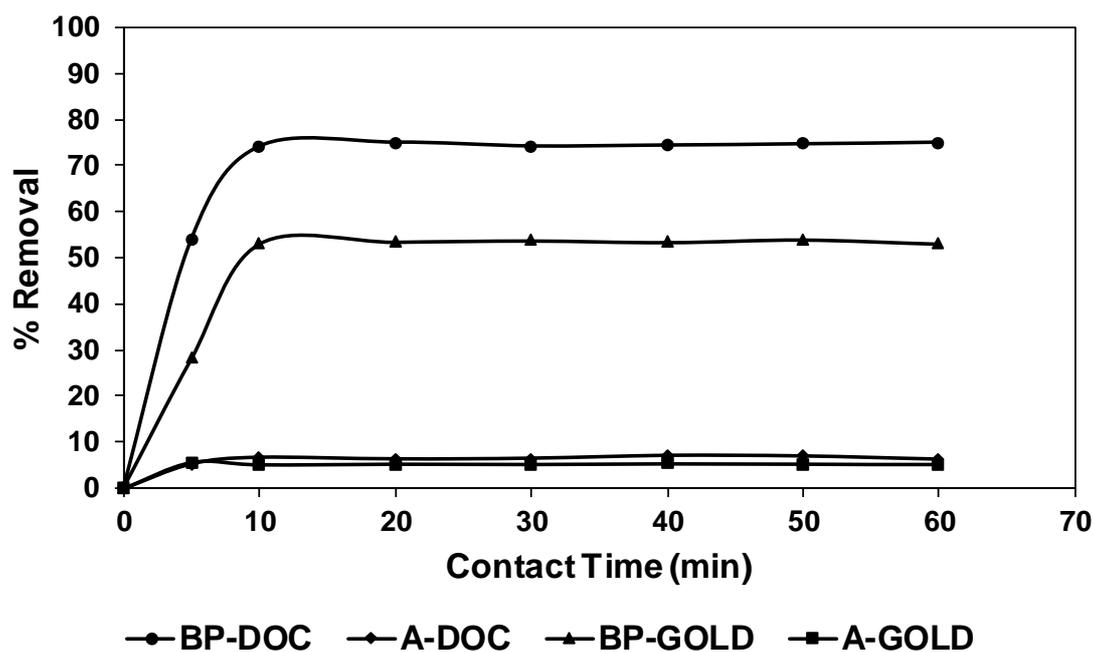


Fig.2. Effect of resin MIEX[®] DOC and MIEX[®] GOLD dosage on removal efficiency in the concentration range from 0.5 to 2 mg/L for Atrazine.

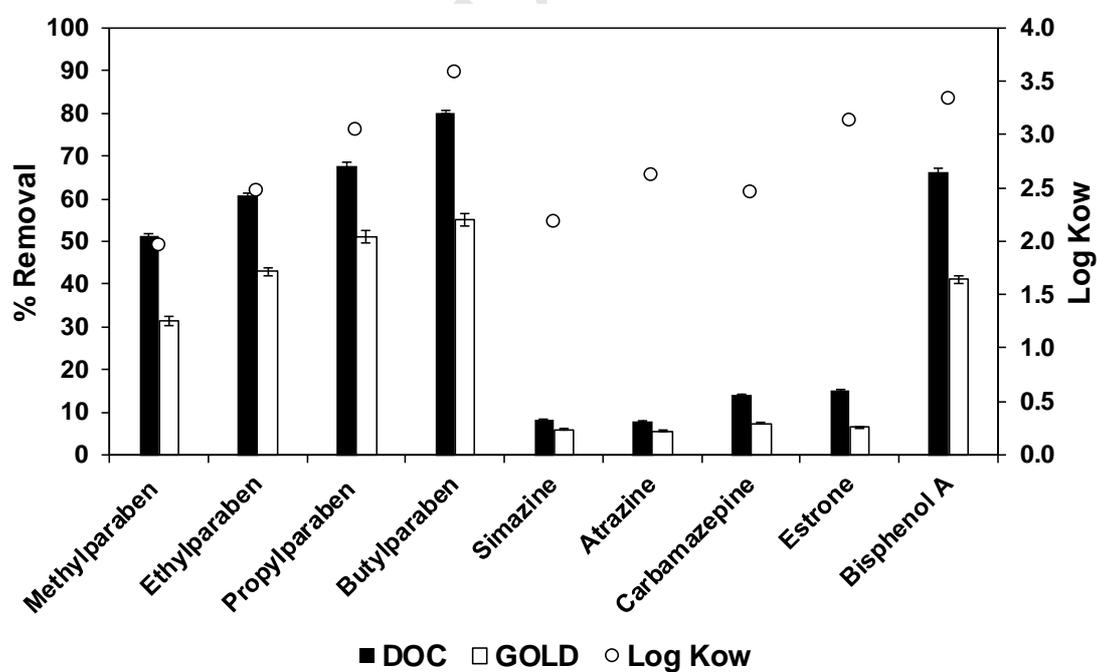
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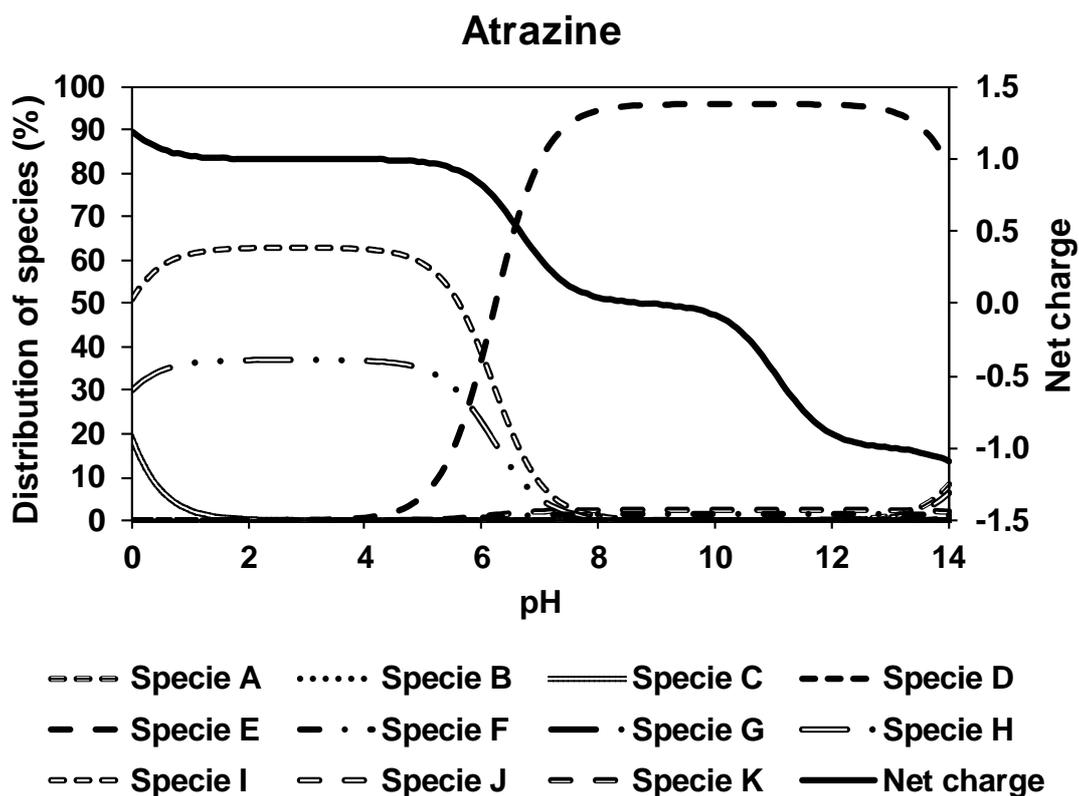
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 743 dosage level of 40 mL/L using both resins (DOC and GOLD).

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745

746 **Fig. 4.** Removal percentages obtained with the MIEX® DOC and MIEX® GOLD resins
 747 for the nine contaminants studied.

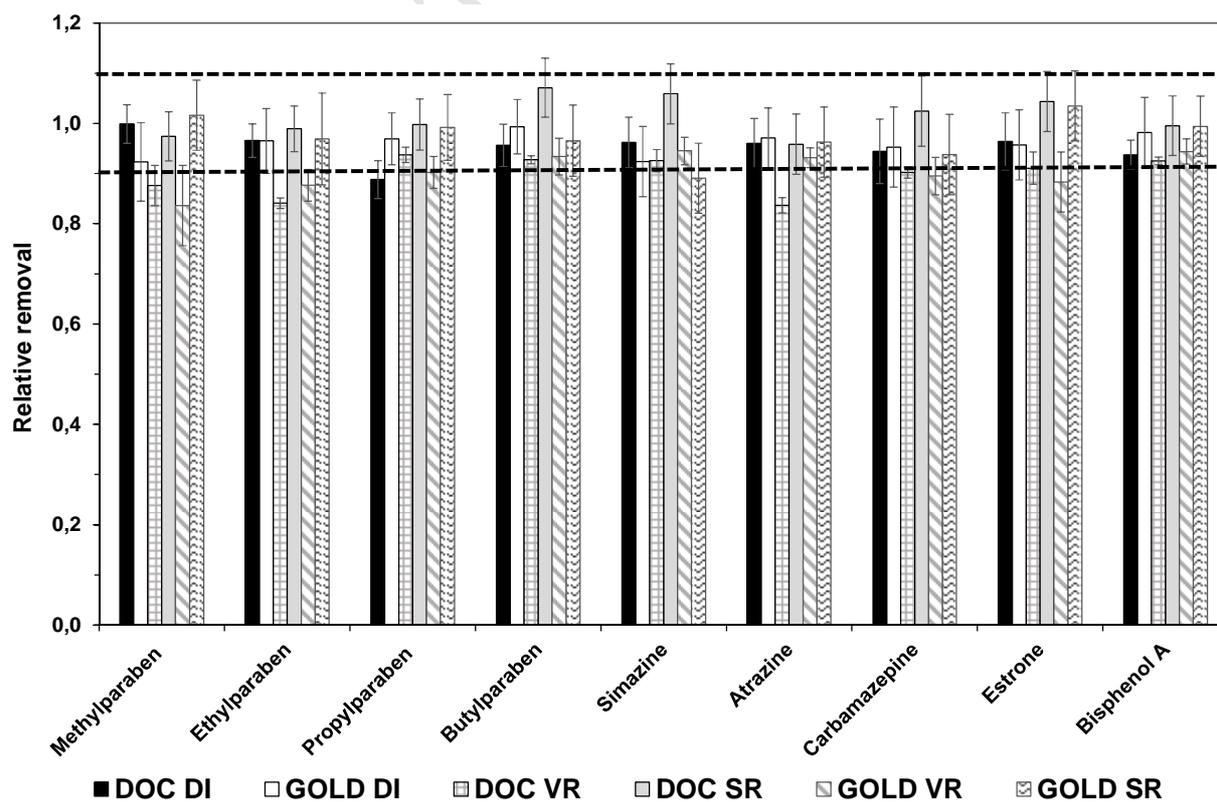


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749 **Fig. 5.** Distribution of species and net charge of atrazine as a function of the pH of the
 750 solution.

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752



753 **Fig. 6.** Relative removal efficiency (\pm SD) obtained for a multi-component solution after
754 treatment with MIEX® DOC and MIEX® GOLD resins. The multi-component solution
755 were prepared with Distilled Water (DI), water from the Verde River (VR) and water
756 from the Segura (SR) River.

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Tables

767 **Table 1.** Physicochemical properties and Calibration parameters of the HPLC-UV
768 method -concentration range of 0.5 to 5 mg/L (coefficients of determination (r^2) and
769 limits of detection (LOD) and quantification (LOQ) for each compound studied).

770

771

772 **Table 1.** Physicochemical properties and Calibration parameters of the HPLC-UV
 773 method -concentration range of 0.5 to 5 mg/L (coefficients of determination (r^2) and
 774 limits of detection (LOD) and quantification (LOQ) for each compound studied).

Compound	MW (g/mol)	Log Kow ^a	pKa ^a	r^2	LOD	LOQ	^a
Atrazine	215.685	2.61	1.60	0.9997	0.153	0.510	^a (Agarwala et al., 2016)
Simazine	201.658	2.18	1.62	0.9997	0.149	0.496	
Bisphenol A	228.291	3.32	9.60	0.9992	0.159	0.353	
Estrone	270.372	3.13	10.3	0.9999	0.092	0.307	
Carbamazepine	236.274	2.45	13.90	0.9999	0.041	0.136	
Methylparaben	152.149	1.96	8.40	0.9999	0.088	0.295	
Ethylparaben	166.176	2.47	8.34	1	0.058	0.193	
Propylparaben	180.203	3.04	7.91	1	0.049	0.163	
Butylparaben	194.23	3.57	8.47	1	0.070	0.233	

679

Figure Captions

680 **Fig. 1.** Effect of resin MIEX® DOC and MIEX® GOLD dosage on removal efficiency in
681 the concentration range from 0.5 to 2 mg/L for Butylparaben.

682 **Fig. 2.** Effect of resin MIEX® DOC and MIEX® GOLD dosage on removal efficiency in
683 the concentration range from 0.5 to 2 mg/L for Atrazine.

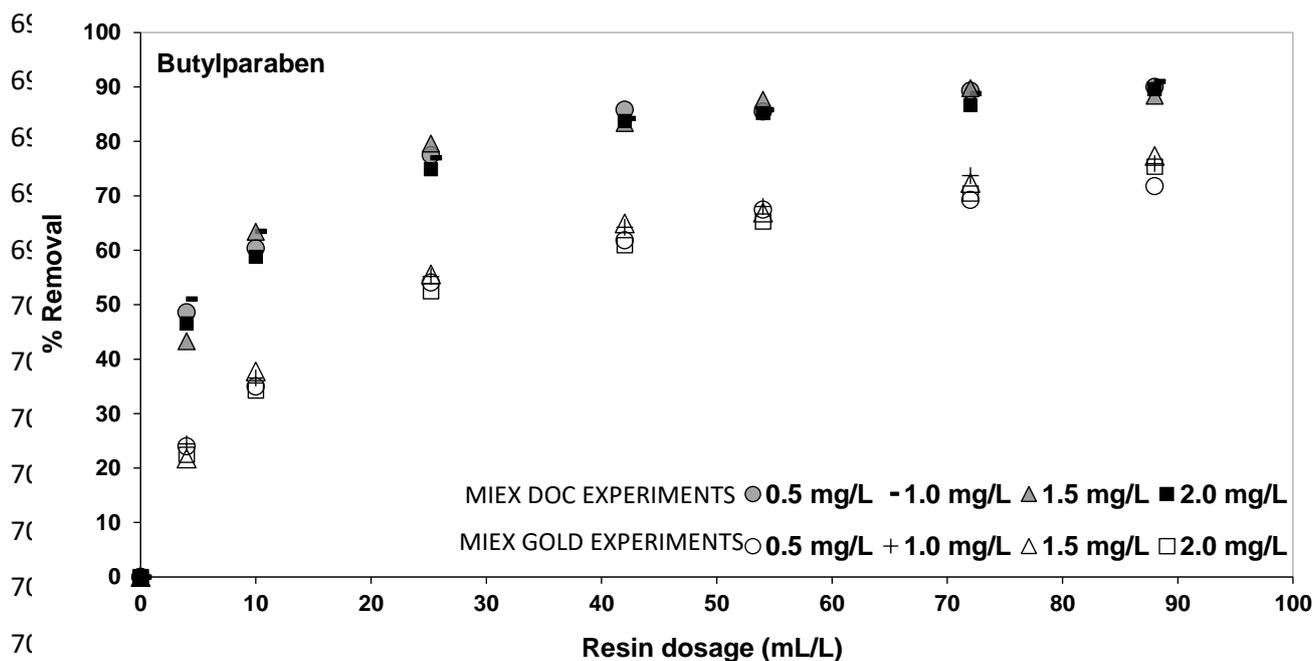
684 **Fig. 3.** Effect of contact time for butylparaben (BP) and atrazine (A) removal using resin
685 dosage level of 40 mL/L using both resins (DOC and GOLD).

686 **Fig. 4.** Removal percentages obtained with the MIEX® DOC and MIEX® GOLD resins
687 for the nine contaminants studied.

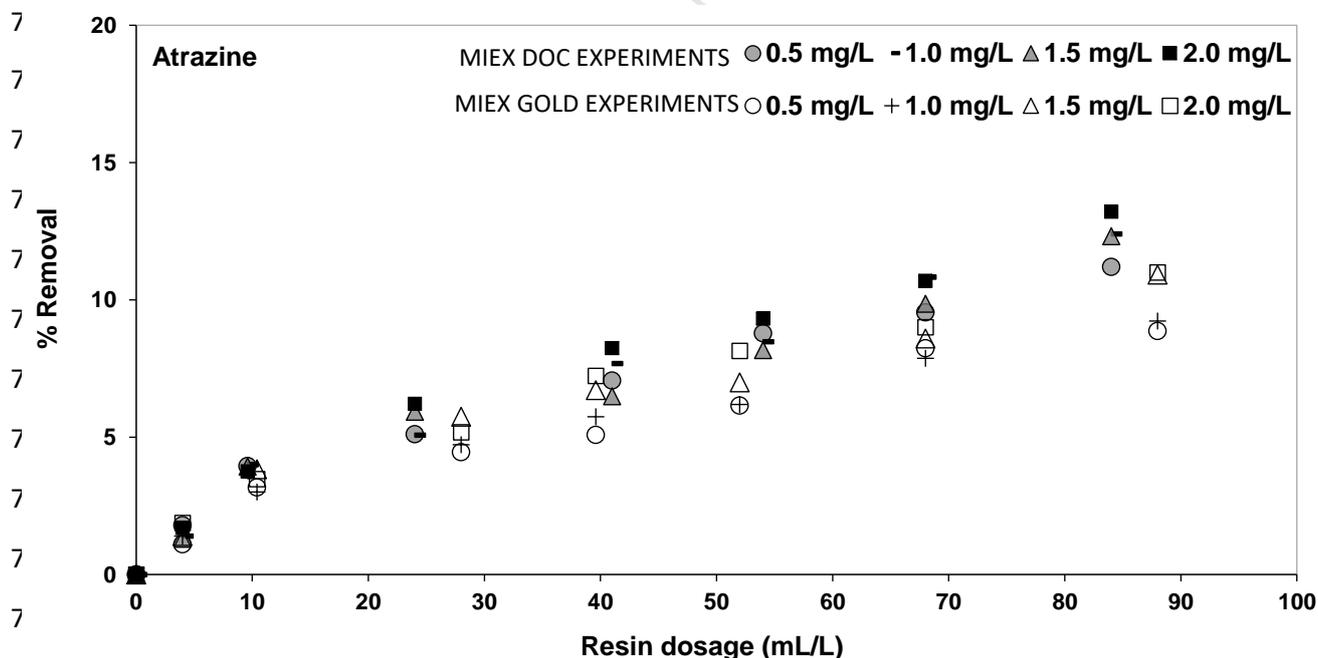
688 **Fig. 5.** Distribution of species and net charge of atrazine as a function of the pH of the
689 solution.

690 **Fig. 6.** Relative removal efficiency (\pm SD) obtained for a multi-component solution after
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693 the Segura (SR) River.

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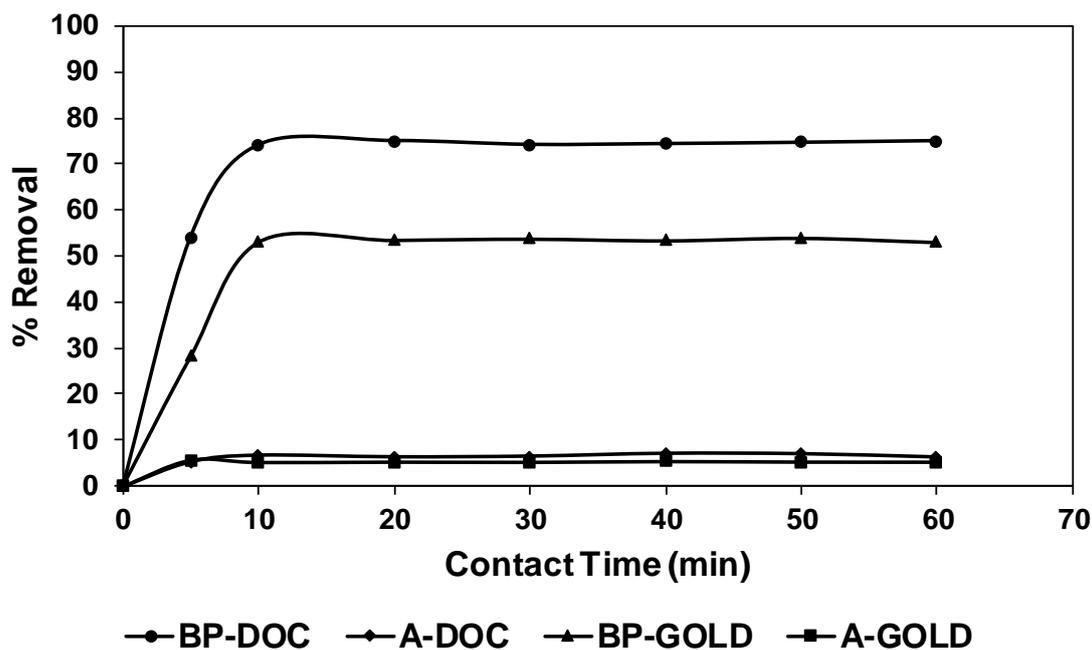
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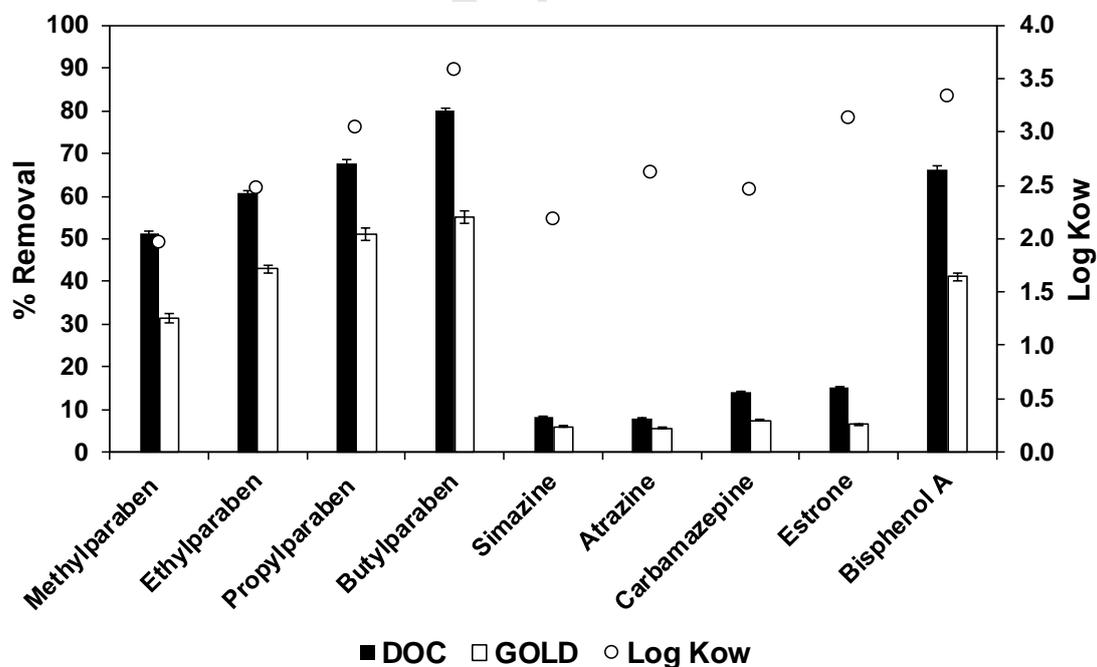
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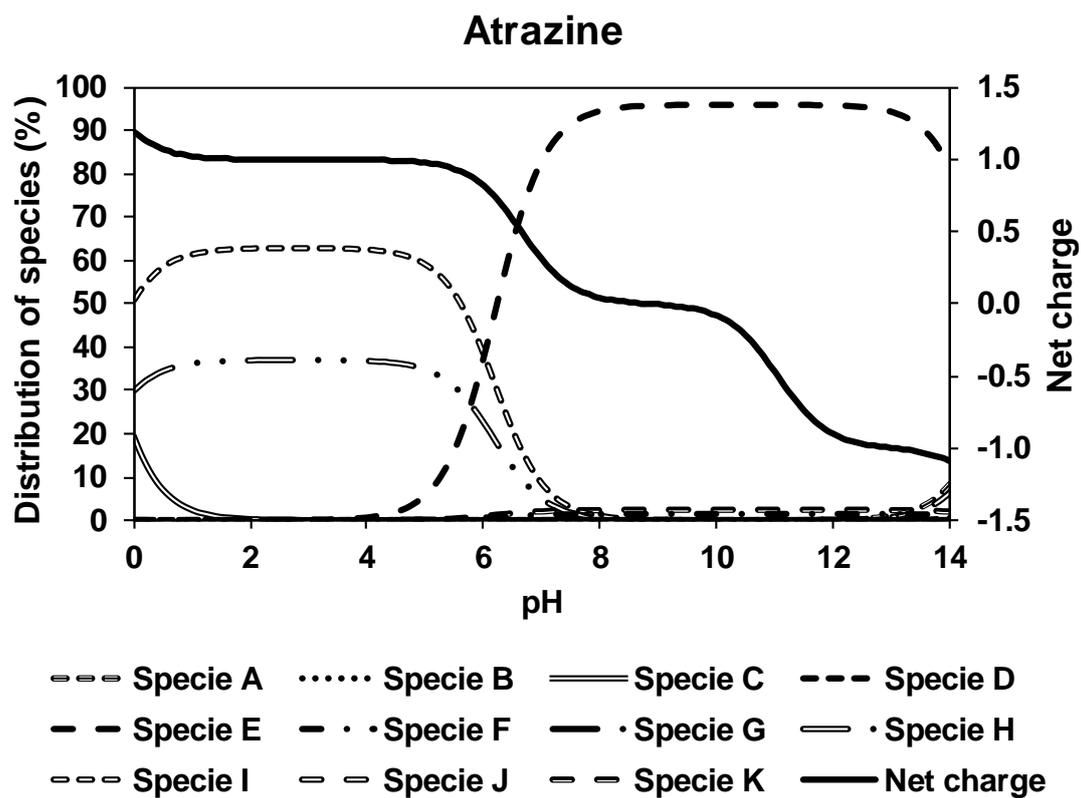
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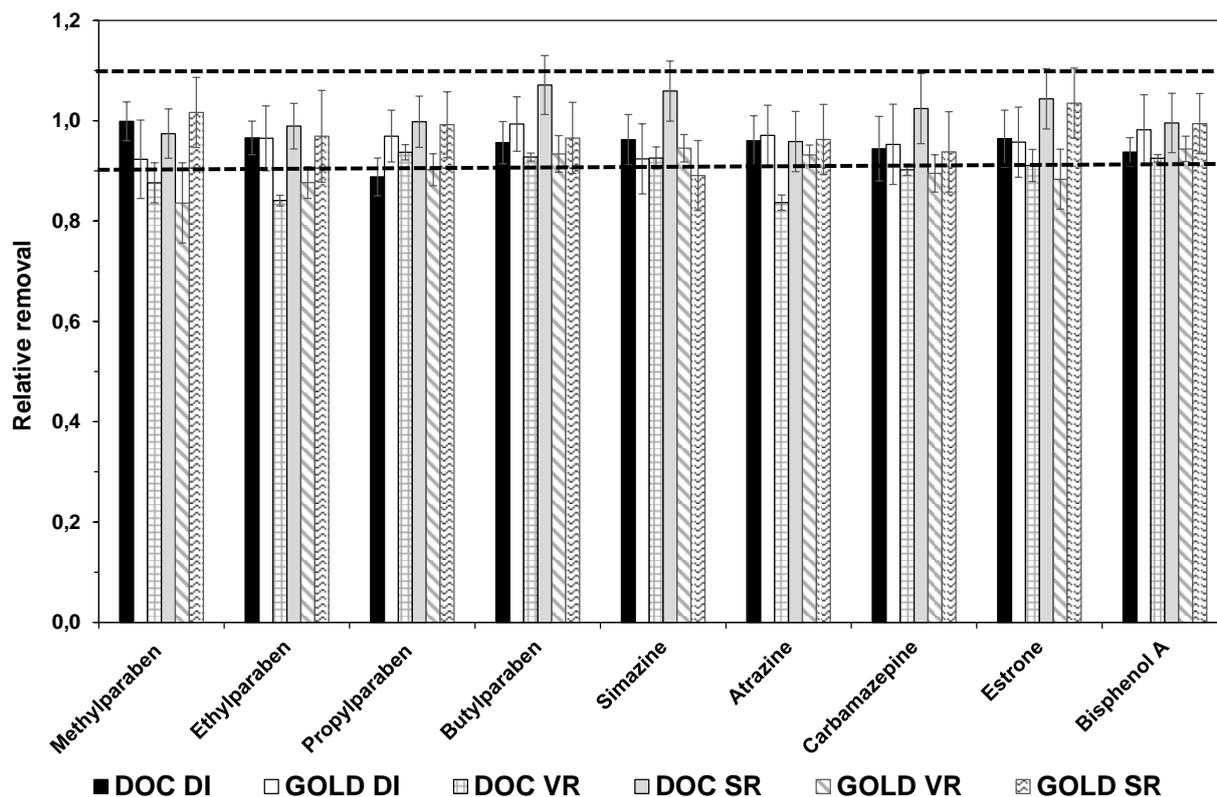


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Butylparaben reached the highest removal efficiency using MIEX DOC resin

Atrazine is the compound that achieved the lowest removal efficiency.

Removal efficiency depended on the physical-chemical characteristics the contaminants

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