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Cyclodextrin polymers and salts: An Eco-Friendly combination to modulate the removal of sulfamethoxazole from water and its release.

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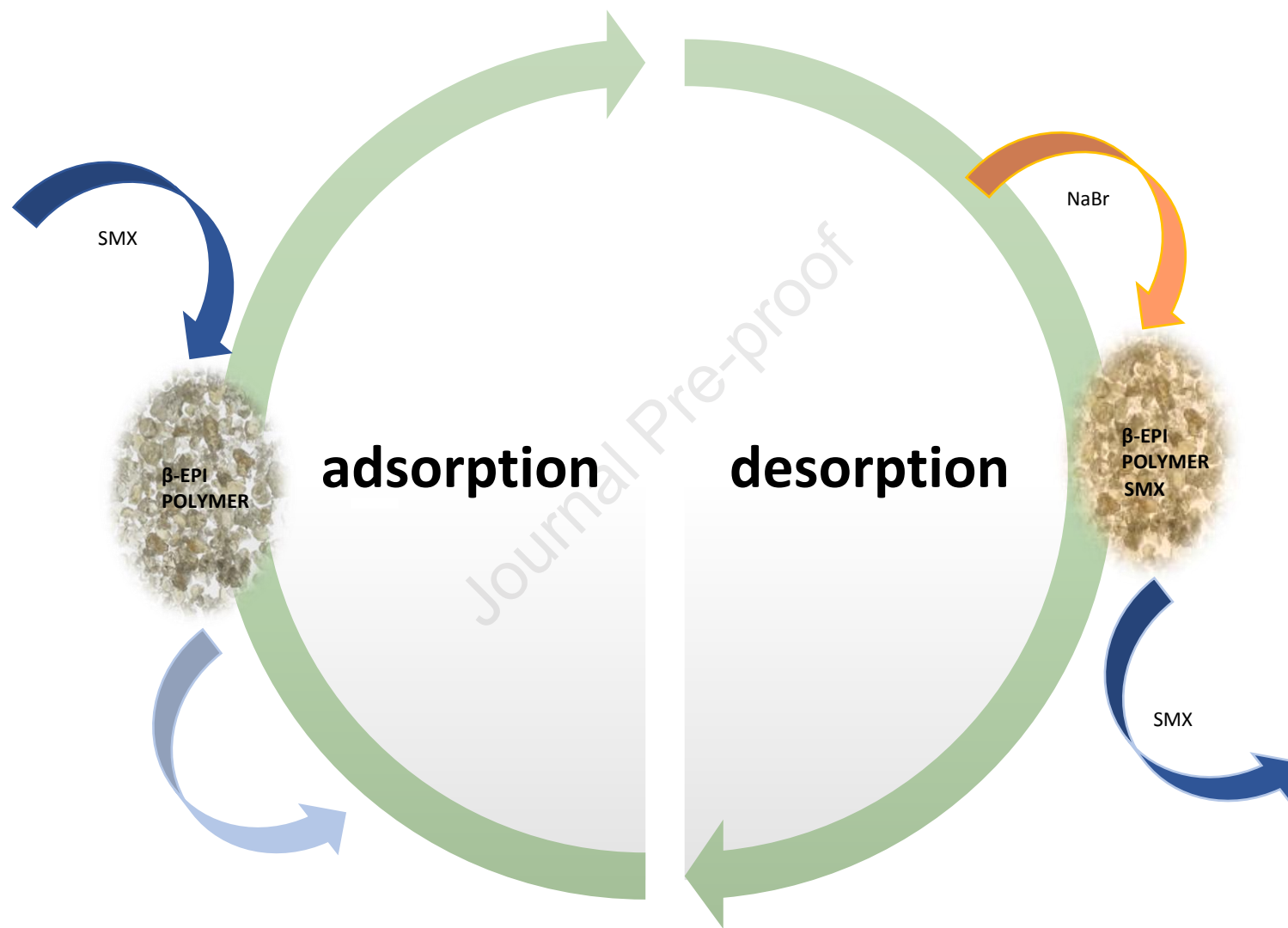
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1 CYCLODEXTRIN POLYMERS AND SALTS: AN ECO-FRIENDLY
2 COMBINATION TO MODULATE THE REMOVAL OF
3 SULFAMETHOXAZOLE FROM WATER AND ITS RELEASE.

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29 Abstract

30

31 This study is aimed to validate water-insoluble cyclodextrin-epichlorohydrin polymer (β -EPI) use to remove,
32 by adsorption, sulfamethoxazole (SMX) from water and then release it via an environmentally friendly
33 treatment so that the adsorbent can be recycled according to one of the objectives of the European Project
34 Life “Clean up” (LIFE 16 ENV/ES/000169).

35 SMX adsorption experiments on β -EPI polymer in-batch were performed, varying different experimental
36 parameters of the process, such as contact time, pH values, and so on.

37 The adsorption process, exothermic and driven by enthalpy, occurs both through the formation of inclusion
38 and association complexes, involves mainly hydrophobic and hydrogen bonds, has a rate-controlling step
39 depending on both pollutant concentration and adsorbent dose and can be described by the Freundlich and
40 Dubinin-Radushkevich models which confirm the polymer surface heterogeneity and the physical nature of
41 the adsorption. The presence of salts gives rise to a general decrease in the SMX sorption, mainly in the case
42 of bromide, which was used to promote the SMX desorption and regenerate the adsorbent. The overall
43 results indicate that β -EPI polymer is not only capable of removing SMX by adsorption with short contact
44 times and a $q_{\max} = 10$ mg/g but it is also easily regenerated using a 0.5 M solution of sodium bromide without
45 any loss in the adsorption performance and with obvious economic and environmental advantages. The
46 polymer as synthesized, with SMX adsorbed and regenerated was characterized by FT-IR, SEM and DSC.

47

48

49 **Keywords:** emerging contaminants; adsorption; cyclodextrin polymers; supramolecular interactions; salt
50 effect; sulfamethoxazole

51

52 1.Introduction

53 Sulfamethoxazole (SMX) is an antibiotic belonging to the class of sulfonamides, antimicrobial
54 drugs with a broad spectrum of activity against gram-positive and certain gram-negative bacteria.

55 SMX use was approved by the U.S. Food and Drug Administration in 1961, and since then, it has

56 been widely used for treating many bacterial infections in both humans and animals. In veterinary
57 science, SMX was also used as a growth promoter until 2006, when its use was banned
58 (Prasannamedha and Kumar, 2020). Despite this reduction in its usage, SMX is still present in the
59 soil, sediments, surface water, and groundwater, and has been detected even in drinking water
60 (Zheng et al., 2020). There are many reasons why SMX is widely found in the environment. First,
61 SMX has high water stability with a DT50 of 51.7 days; secondly, one of its metabolites, N4-
62 acetylsulfamethoxazole, tends to re-transform itself into the parent compound, and most of the
63 Waste Water Treatment Plants (WWTPs) are inefficient in removing this contaminant.

64 The main hazard associated with the presence of SMX in surface water, unlike other emerging
65 contaminants (EPs), is not due to bioaccumulation, which has been demonstrated to be poor, but in
66 generating bioma antibiotic resistance according to a well-known mechanism: initially, aquatic
67 microorganisms become antibiotic-resistant, then they produce antibiotic-resistant genes that, if
68 present in transferable genes, make other microorganism antibiotic-resistant, including human
69 pathogens (Grenni et al., 2018).

70 Developing sustainable technologies that allow efficient removal of EPs in general and SMX, in
71 particular, is, therefore, an emergency need, as highlighted by 3 of the 17 Sustainable Development
72 Goals of the 2030 UN Agenda. In fact, the improvement of the quality of water coming out from the
73 WWTPs is crucial to reduce the number of deaths and illnesses from hazardous chemicals and
74 water contamination (goal 3), to achieve universal and equitable access to safe and affordable
75 drinking water for all, to protect water-related ecosystems (goal 6) and to prevent and reduce marine
76 pollution in particular from land-based activities (goal 14). Many of the proposed technologies are
77 based on the adsorption process, which has the advantage of being easily integrated into existing
78 WWTPs and does not give rise to the formation of toxic by-products. The efficiency of the
79 adsorption process depends on the characteristics of the adsorbent, adsorbate, and also water to treat
80 (pH, presence of salt or other pollutants, etc.). Since the characteristics of the contaminant that is to

81 be adsorbed and the water characteristics in which it is present, can hardly be controlled or chosen,
82 great attention is paid to the adsorbent material development and choice.

83 This process's economic and environmental cost depends mainly on the type of adsorbent material
84 chosen and, therefore, its factors of production, its lifetime, possibility, and regeneration mode.

85 Materials like activated carbon of different derivation, biochars, graphene and its derivatives,
86 carbon nanotubes, polymeric substances, and minerals have been used singularly or in combination
87 as adsorbent material for SMX (Prasannamedha and Kumar, 2020; Wang et al., 2020; Zheng et al.,
88 2020). These performances of these materials mainly depend on the adsorption capacity and the
89 contact time necessary to reach the adsorption equilibrium. Unfortunately, the adsorption process of
90 SMX on most of these materials is slow, and long contact times are necessary. For example, Li and
91 Quan (2017) found that nanoporous carbons derived from metal-organic frameworks can adsorb
92 SMX after 10 hours of contact time with the aqueous solution (Li and Quan, 2017). Data published
93 by Çalışkan and Göktürk (2010) showed that coal-based activated carbon allows the adsorption of
94 about 55% of SMX from aqueous solutions within approximately 5 hours (Çalışkan and Göktürk,
95 2010). As reported by Moral-Rodríguez et al. (2016), by using F400 granular activated carbon to
96 remove SMX from water, it takes more than 90 hours to reach the equilibrium and the SMX
97 concentration breakdown in solution is around 80% (Moral-Rodríguez et al., 2016).

98 Most of these materials cannot be regenerated or require the use of environmentally unsustainable
99 treatments such as the extraction with organic solvents (Zheng et al., 2020). Also, the use of low-
100 cost adsorbent available in large quantities, although renewable and inexpensive, has the problem of
101 disposal after the use. All these matters, along with the long contact time requested by the
102 adsorption process, hamper large scale applications.

103 Here we report the results of a study on the removal of SMX from water using as adsorbent
104 material, a water-insoluble cyclodextrin-epichlorohydrin polymer already tested and validated for
105 the removal of a wide variety of emerging contaminants from water (Gómez-Morte et al., 2021;
106 Romita et al., 2019). For example, it was demonstrated that over 70% of atrazine 2 mg/L can be

107 removed from the water within only 1 hour of contact time with the polymer (Romita et al., 2019).
108 Excellent results were also obtained for the treatment of textile industry wastewater, subject of the
109 LIFE + European project, DYES4EVER (Pellicer et al., 2018, 2019; V. Rizzi et al., 2019; Semeraro
110 et al., 2015). The use of CD-EPI polymers has made it possible to remove dyes from the wastewater
111 only after 30 minutes of contact and their subsequent release and reuse of both clean water and dyes
112 for other industrial processes.

113 Cyclodextrins (CDs) are very effective for water remediation applications, thanks to their ability to
114 form inclusion complexes with organic molecules through weak interactions ruled by
115 supramolecular chemistry (Agostiano et al., 2002; Fini et al., 2004; L. Dentuto et al., 2005; Rizzi et
116 al., 2016; Semeraro et al., 2015). The cross-linking of CDs with epichlorohydrin (1-chloro-2,3-
117 epoxypropane, EPI) enables the formation of ramified polymers, which can adsorb emerging
118 pollutants from water solutions very efficiently, thanks also to their relatively high cross-linking
119 density and their interesting swelling properties (Ning et al., 2009).

120 In this research work, in-batch SMX adsorption experiments onto a β -cyclodextrin-epichlorohydrin
121 polymer (β -EPI) were performed varying different experimental parameters of the process, such as
122 contact time, pH values, and so on. The influence of several inorganic salts on the adsorption process
123 was also assessed to understand better the nature of supramolecular interactions involved and to
124 learn how to use salts to modulate them in order to be able, “on demand”, to increase the efficiency
125 of adsorption, requisite for quantitative removal of the SMX from the water, or to promote its
126 desorption, indispensable for the regeneration of the material. To the best of our knowledge this
127 study is the first case of regeneration of material able to adsorb SMX by an environmentally
128 friendly approach and without the use of other pollutants such as, for example, organic solvents
129 reported in literature.

130 **2. Materials and methods**

131 **2.1 Chemicals**

132 All chemicals used were purchased from Sigma Aldrich, except for sodium bromide and sodium

133 perchlorate, provided by Carlo Erba. Aqueous sulfamethoxazole solutions were prepared by
134 dissolving appropriate quantities of analytical-grade powder (Sigma Aldrich) in deionized water.

135 ***2.2 β -cyclodextrin-epichlorohydrin polymer synthesis***

136 The β -CD polymer synthesis is based on the procedure described by Pellicer et al. (2018), with
137 some modifications.(Pellicer et al., 2018) 24 g of CD and 60 mg of sodium borohydride were
138 dissolved in 24 mL of deionized water under magnetic stirring at 50°C, then 42 mL of
139 epichlorohydrin were added dropwise to this mixture, maintaining the system under agitation at
140 50°C for 5 hours. Once the reaction was completed, the so formed gel underwent four washing
141 cycles in the following order: acetone, water, water, and acetone. Then, the product was dried at
142 50°C overnight in an oven, and the resulting solid was ground in a mortar. In order to neutralize the
143 polymer, two washing steps were performed: firstly with 100 mL of a 10^{-2} M HCl solution (25
144 grams of ECP per liter of water), then decanted, rewashed with deionized water (25 grams of ECP
145 per liter of water) and decanted again. Finally, ECP was dried at 50°C overnight and ground into
146 fine particles.

147 ***2.3 Scanning electron microscopy (SEM)***

148 The surface morphology of β -EPI polymer was investigated using FEI Quanta FEG 250. Samples
149 were placed on an aluminum stub.

150 ***2.4 In-batch adsorption and desorption experiments***

151 The adsorption experiments were carried out in batch mode using a fixed volume (15 mL) of SMX
152 solution, having appropriate concentrations (from 1.3 to 15 mg/L), with a predetermined amount of
153 adsorbent (from 3.13 to 25 mg/L) under continuous magnetic stirring at 170 rpm rate. The
154 maximum contact time set between the adsorbent and the adsorbate was 60 minutes. Aliquots of the
155 batch mixtures were withdrawn at specific times and centrifuged at 14000 rpm for 8 minutes, then
156 the residual SMX concentration in the supernatants was evaluated by UV-Vis spectrophotometric
157 measurements.

158 The percentage of SMX removal from the water was calculated by using equation (1):

$$SMX \text{ adsorption } \% = \frac{C_0 - C_t}{C_0} \cdot 100\% \quad (1)$$

159

160

161

162 where C_0 and C_t are the SMX concentrations (mg/L) before and after the adsorption test. The
163 adsorption process was also investigated at different pH values within the range 2.0–12, at different
164 temperatures (293, 313 and 333 K) and in presence of different concentration of NaCl (0.1-1.5 M),
165 $MgCl_2$ (0.05 - 0.5 M), $CaCl_2$ (0.05 - 0.5 M), NaBr, $NaClO_4$ and Na_2SO_4 0.1 M.

166 In order to evaluate the maximum capacity of β -EPI to adsorb SMX, consecutive cycles of SMX
167 adsorption were performed. After reaching equilibrium, the same polymer was reused to adsorb the
168 pollutant from another solution at the same concentration for the same contact time; consecutive
169 cycles of adsorption were performed up to reach a saturation status.

170 *In-batch* SMX desorption experiments of SMX were also performed by extraction with NaBr
171 aqueous solutions having concentrations within 0.1 - 1.0 M. The preliminary adsorption
172 experiments were carried out in the absence of salt at the same experimental conditions described
173 above. After reaching the equilibrium, the adsorbent was isolated and washed with abundant
174 deionized water to remove SMX molecules aspecifically adsorbed onto the polymer. The excess of
175 water was removed through centrifugation at 14000 rpm for 8 minutes, then the polymer was
176 dispersed into 15 mL of a sodium bromide aqueous solution having a specific concentration, and the
177 system was maintained under constant magnetic stirring at 170 rpm for the contact time desired.
178 SMX concentration in water was evaluated by absorbance measurements, and all the desorption
179 percentages were calculated by using equation 2:

180

$$\% \text{ desorption} = \frac{W_{des}}{W_{ads}} \cdot 100\% \quad (2)$$

182

183 where W_{des} e W_{ads} are the amounts of SMX desorbed and adsorbed, respectively.

184 **2.5 UV-Visible and FT-IR spectroscopic measurements**

185 UV- Vis absorption spectra were recorded using a Varian CARY 5 UV-Vis-NIR spectrophotometer
186 (Varian Inc., now Agilent Technologies Inc. Santa Clara, CA, USA). SMX external calibration was
187 performed by using aqueous solutions ranging from 1.3 to 15 mg/L at 257 nm.

188 FTIR-ATR spectra were recorded within 600-4000 cm^{-1} range using a Fourier Transform Infrared
189 spectrometer 670-IR (Varian Inc., now Agilent Technologies Inc. Santa Clara, CA, USA) whose
190 resolution was set to 4 cm^{-1} . 32 scans were summed for each acquisition.

191 **2.6 Differential Scanning Calorimetry (DSC)**

192 The thermal properties of the β -EPI polymer after different cycles of adsorption/desorption were
193 investigated by DSC (Q200 TA Instruments) under a nitrogen flow of 50 mL/min at the heating rate
194 of 10 $^{\circ}\text{C}/\text{min}$ from 0 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$.

195

196 **3. Results and discussion**

197 The morphological characteristics of the β -cyclodextrin-epichlorohydrin polymer, used as an
198 adsorbent in this study, have been investigated through microscope analyses. The results (**Figure**
199 **S1**) indicate that the adsorbent's surface is rough and irregular, with large pores randomly
200 distributed. Hence this material has the important key features to be used for pollutant adsorption
201 from wastewater.

202 **3.1 Adsorption of SMX onto β -EPI polymers**

203 Since one of the aims of this study is to learn how to increase the efficiency of the adsorption
204 process of SMX onto β -EPI polymers, the dependence of this process on operational parameters
205 such as contact time, adsorbent dose, initial SMX concentration, temperature, and pH was studied.
206 The results obtained by each set of experiments, performed varying experimental parameter one by
207 one along with the contact time, are reported in **Figure 1a, 1c, 1e, and 1g**.

208

209

Figure 1

210

211 All graphs show that the adsorption equilibrium was reached after only 10 minutes of contact
212 between the adsorbent material and the solution. The maximum adsorption efficiency obtained at
213 room temperature, using an SMX solution at a concentration of 10 mg/L in the presence of 25
214 mg/mL of polymer is 61.7%, which means that the residual SMX concentration in solution is 3.83
215 mg/L.

216 Such a short equilibrium contact time is very advantageous for emerging pollutants removal from
217 treated water on industrial scale, where the decontamination process should be as rapid as possible.
218 **Figure 1b** shows that at increasing the SMX concentration from 1.3 to 15 mg/L, using 25 mg/L of
219 polymer, the adsorption amount increases from 47.3% to 73.7%, suggesting the molecular diffusion
220 has an important role in the adsorption process.

221 The plot reported in **Figure 1d** clearly shows a typical dose adsorbent effect: increments of the
222 polymer amount give rise to an increase of SMX removal efficiency since there are more available
223 sites on the adsorbent to interact with the adsorbate.

224 At increasing of the temperature from 293 to 333 K (**Figure 1f**), the SMX adsorption (10 mg/L
225 SMX/25 mg/L β -EPI polymer) decreases from 78.1% to 27.0%, as already observed studying the
226 adsorption of atrazine on the same material. This trend could indicate the adsorption process's
227 exothermicity, as reported in the thermodynamic data section. This dependence of the adsorption on
228 the temperature is advantageous because it permits the reduction of the energy consumption and
229 problems associated with this.

230 Among the various operating parameters considered, the pH is the one that has the most significant
231 effect on the amount of SMX adsorbed. Data in **Figures 1g** and **1h**, obtained using a 10 mg/L of
232 SMX solution, 30 min as contact time, and 25 mg/L of the β -EPI polymer at room temperature,
233 suggest that the percentage of adsorption increases at decreasing of the pH values. A similar trend
234 in the pH range 4.2-10.5, followed by a decrease at pH lower than 4.2, has been observed studying

235 the dependence of adsorption on pH of SMX on porous carbons (Zheng et al., 2020), a material
236 having an isoelectronic point at pH 4.2.

237 As already reported in the literature, SMX has two pK_a values at 1.6 and 5.7 and consequently,
238 depending on the medium pH, can exist in three forms, cationic, neutral, and anionic. In the
239 aqueous solution at neutral pH, SMX is present mainly in its anionic form (SMX^-) due to the
240 deprotonation of the amino-group belonging to the sulfamidic functionality (Chen et al., 2014). At
241 pH values between pK_{a1} and pK_{a2} , such as pH 4, SMX is almost all in the neutral form, whereas at
242 pH lower than 1.6, that is pK_{a1} , the cationic form of SMX prevails since the aniline amino group is
243 protonated (**Figure 1h**).

244 Unlike SMX, the polymer remains unchanged when pH changes and does not acquire any charge in
245 the pH range 2-12 (Romita et al., 2019). Therefore, it is not possible to rationalize the dependence
246 of adsorption efficiency of SMX on pH exclusively in terms of repulsions or electrostatic attractions
247 as done in the case of SMX adsorption on Activated Carbon (Prasannamedha and Kumar, 2020). It
248 is necessary to consider that β -EPI polymer has a complex structure, made by cyclodextrins linked
249 by glyceryl bridges and glycerol mono ether side chains, bearing many hydroxyl groups. Data in
250 **Figure 1h** indicate that the uptake is maximum in the pH range between pK_{a1} and pK_{a2} , where the
251 neutral form of SMX prevails. In this form, SMX can diffuse in the polymer network and interact
252 with cyclodextrins forming inclusion complexes and/or interact with moieties present in the
253 polymer's three-dimensional structure, forming association complexes.

254 The dependence of the SMX adsorption percent on pH suggests that the interactions between SMX
255 and β -EPI polymer are mainly hydrophobic and due to hydrogen bond formation. The contribution
256 of hydrophobic interactions to adsorption is in accordance with the partial hydrophobic character of
257 the SMX, as shown by the almost unitary value of its octanol-water partition ratio, $\log K_{ow} = 0.89$
258 (Amézqueta et al., 2019; Nguyen Dang Giang et al., 2015). The hydrogen bonds form among the
259 groups containing oxygen and nitrogen, which are hydrogen-donor and/or -acceptor, and belong to
260 the pollutant (Anilinic, Sulfamidic and isoxazolyl groups), to the polymer (glyceryl, glycerol mono

261 ether, and hydroxyl groups), and to water. FT-IR data (**Figure S2**) support these claims. No
 262 adsorbed SMX leaching was observed at longer contact time with an SMX solution unlike that
 263 observed by putting the polymer with adsorbed SMX in contact with water where a moderate
 264 release of less than 20% of the SMX is observed. This leaching, credibly by molecules more weakly
 265 bound to the adsorbent, can be advantageously used in the process of regeneration of the adsorbent
 266 polymer.

267

268 **3.2 Adsorption kinetics**

269 The kinetics of SMX adsorption on β -EPI polymer was studied using the Lagergren pseudo-first
 270 and pseudo-second-order kinetic model along with the Weber Morris intraparticle diffusion model
 271 (Rizzi et al., 2020; Romita et al., 2019). The analysis was carried out both by changing SMX
 272 concentration, fixing the adsorbent amount, and vice versa.

273 Since the linear coefficient of determination (R^2) obtained by applying the pseudo-first-order kinetic
 274 model is lower than 0.5, only data obtained applying the second-order kinetic to experimental data
 275 are plotted in **Figure 2** as a function of SMX concentration (**Figure 2a**) and β -EPI polymer dose
 276 (**Figure 2b**).

277

Figure 2

278

279 Experimental data were fitted using the pseudo-second-order kinetic model equation:

280

$$281 \quad \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (3)$$

282

283 where q_e and q_t are the SMX concentration adsorbed at equilibrium ($\text{mg} \times \text{g}^{-1}$), and at time t (min)
 284 respectively, and k_2 is the pseudo-second-order rate constant ($\text{g} \times \text{mg}^{-1} \times \text{min}^{-1}$).

285 q_e and k_2 values obtained by the linear fitting of t/q_t vs. time are reported in **Table 1**, along with the
 286 experimental values of q_e and the corresponding coefficient of determination.

287

288

Table 1

289 The near coincidence between the experimental q_e values and those obtained by regression confirms
 290 that the second-order kinetic model well describes the adsorption process of the SMX on the
 291 polymer and that, therefore, the rate-controlling step depends on both pollutant concentration and
 292 adsorbent dose. Besides, the decrease of the kinetic constant k_2 as the SMX concentration increases
 293 (**Table 1**) indicates that diffusion of SMX from the bulk solution to the polymer's surface is not the
 294 rate-determining step of the adsorption process. The increase of the kinetic constant k_2 at increasing
 295 of the polymer dose suggests a direct involvement of polymer active sites in the slowest process
 296 step.

297

Figure 3

298 Additional information was obtained using the Weber-Morris model (Weber and Morris, 1963) to
 299 analyze the dependence of q_t on $t^{1/2}$ (**Figure 3**) at the beginning of the adsorption process, that is,
 300 for which the condition $q_t/q_e < 0.4$ is fulfilled (Obradovic, 2020).

301 This model, also known as the intra-particle diffusion model (IPD), is described by the following
 302 equation:

303

$$304 \quad q_t = k_{IPD} \cdot t^{1/2} + C \quad (4)$$

305

306 where k_{IPD} ($mg \times g^{-1} \times min^{-1/2}$) is the kinetic constant related to the intra-particle diffusion rate,
 307 and C is a constant and can be obtained by plotting q_t on $t^{1/2}$ (**Figure 3**). According to this model, if
 308 the plot of q_t vs. $t^{1/2}$ is linear and passes through the origin, the intraparticle diffusion is the rate
 309 controlling step. If, as in this case, despite having a linear trend, this does not pass through the

310 origin, the slow stage is more complex and does not concern only the intraparticle diffusion (Özcan
311 and Özcan, 2005).

312 **3.3 Adsorption isotherm**

313 The q_e (mg/g) dependence on c_e (mg/L), where q_e is the amount of SMX adsorbed onto the solid
314 and c_e is the equilibrium concentration of the SMX in solution, was analyzed using the equilibrium
315 isotherm equations associated with the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich
316 models. As already observed studying the adsorption of other contaminants on water-insoluble
317 cyclodextrin epichlorohydrin polymers, the Freundlich model fits better experimental data with a
318 coefficient of determination higher than 0.85 (**Table S1**). The values of n evaluated by the fitting
319 are associated to the degree of curvature of the Freundlich isotherm. The obtained $1/n$ values, higher
320 than 1, indicating that when the concentration of chemical under investigation increases, the relative
321 amount adsorbed increases, are consistent with the dependence of the adsorption percentage on
322 SMX concentration (figure 1 b).

323 In addition to the Freundlich model, also the Dubinin-Radushkevich (D.R.) model fits data but with
324 a lower coefficient of determination which is between 0.70 and 0.80 depending on the temperature
325 (**Table S1**). The K_{D-R} (mol^2/J^2) values were used to evaluate the mean adsorption energy which,
326 being <8 KJ/mol at all temperatures, allowed us to assess the physical nature of the adsorption
327 process (Rizzi, 2019).

328 Other models, Langmuir and Temkin, do not fit experimental data, hence they are not suitable to
329 describe the adsorption process. These results confirm the polymer surface's heterogeneity and that
330 SMX is physisorbed on the polymer both through the formation of inclusion and association
331 complexes.

332 **3.4 Consecutive cycles of SMX adsorption**

333 Since the Langmuir isotherm adsorption model did not allow us to estimate the maximum
334 adsorption capacity of β -EPI polymer, an experimental determination of this parameter was
335 attempted by performing consecutive cycles of SMX adsorption. The obtained results indicate that,

336 in these adsorption cycles, the polymer performance decreases only slightly until reaching a
 337 saturation status, corresponding to a $q_{\max} = 10$ mg/g confirming the applicative potential of this
 338 adsorbent material. This q_{\max} value, in good agreement with that obtained using as adsorbent
 339 cyclodextrin-based nanosponges (Rizzi et al., 2021), indeed, while being lower than q_{\max} obtained
 340 using activated carbons is higher than those got with biochars and was obtained using a contact time
 341 of a few minutes against the contact times of several hours or days required by other adsorbents
 342 (Prasannamedha and Kumar, 2020; Wang et al., 2020; Zheng et al., 2020).

343 **3.5 Adsorption Thermodynamics**

344 Experimental data at equilibrium at different temperature were used to calculate the equilibrium
 345 constants (K_{eq}) along with the corresponding Gibbs free energy changes (ΔG°) (kJ mol^{-1}) using the
 346 following equations:

$$347 \quad K_{eq} = \frac{q_e}{c_e} = \frac{c_0 - c_e}{c_e} \cdot \frac{V}{m} \quad (5) \quad \text{and } R \text{ is the gas constant. The enthalpy change } (\Delta H^\circ)$$

348 ($\text{kJ} \times \text{mol}^{-1}$) and the entropy variation (ΔS°) ($\text{J} \times \text{mol}^{-1} \times \text{K}^{-1}$) were evaluated by the fitting of ΔG° vs. T
 349 through the equation below:

$$350 \quad \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

353 Thermodynamic data of SMX adsorption onto the β -EPI polymer reported in **Table 2** indicate that
 354 the adsorption process is spontaneous, exothermic, produces an increase of the order degree, and is
 355 based on the interaction of physical nature.

356 **Table 2**

357 **3.6 Effect of salts**

358 The effect of salt on SMX adsorption onto β -EPI was studied using sodium chloride as model salt at
 359 different concentrations (0.05, 0.1, 0.5, 1, and 1.5 M) in 15 mL of SMX 10 mg/L solutions
 360 containing NaCl and 375 mg of β -EPI.

361 As shown in **Figure 4**, the presence of NaCl causes a general decrease in the sorption of SMX,
362 following the order $0\text{ M} > 0.10\text{ M} > 0.50\text{ M} > 1.50\text{ M} > 1.0\text{ M}$.

363

364

Figure 4

365

366 The changes in the sorption efficiency at increasing of salt concentration can usually be explained
367 by considering the salt's possible effects on the adsorbate, adsorbent, and water. Regarding the
368 adsorbate, it is possible the formation of ion pairs between SMX^- and Na^+ which increase the
369 hydrophobicity of the pollutant and therefore its affinity towards the adsorbent. As regards the
370 adsorbent, Na^+ cations and Cl^- anions could interact with the hydroxyl groups of the polymer
371 through ion-dipole forces subtracting active sites of the material to SMX. In addition to these effects
372 due to an ion direct participation, the salt's presence in solution also produces changes in water
373 properties giving rise to different phenomena such as a decrease of the dielectric constant and
374 having NaCl chaotropic properties, also a partial water structure breaker (Fini et al., 2003; Gavish
375 and Promislow, 2016).

376 At the lowest NaCl concentration, 0.10 M, the possible effects might not be significant or
377 counterbalance each other so that, there are no significant changes in the performance of the system
378 if compared with the case of no salt added. At intermediate NaCl concentrations, 0.50 and 1.00 M,
379 specific ion effects are present: it is likely that there is a competition between ions, Na^+ and Cl^- , and
380 SMX molecules in interacting with polymer's active sites, which makes the adsorption less favored
381 (Kunz, 2010). At a high NaCl concentration, 1.50 M, a salting-out effect is observed (Kunz, 2010).
382 In other words, high amounts of salt cause a decrease in the pollutant solubility in water: this could
383 explain why the SMX adsorption efficiency of β -EPI increased from around 28% at 1 M NaCl to
384 about 43% at 1.50 M NaCl. The SMX sorption efficiency decrease is also observed in the presence
385 of LiCl and KCl (data unshown). The differences obtained using the three monovalent ions are not

386 relevant, and hence no systematic correlation has been observed between the experimental results
387 and salt properties.

388 In order to have more information about the salt effect, analogous experiments were performed
389 using magnesium chloride hexahydrate and calcium chloride at the following concentrations: 0.05,
390 0.10, and 0.50 M.

391 **Figure 5**

392
393 The presence of MgCl_2 in the solution provokes slight changes in the adsorption efficiency (**Figure**
394 **5A**). At the lowest MgCl_2 concentrations, 0.05 and 0.1 M, as already observed in the case of NaCl,
395 experimental results obtained in the presence of salt are almost identical to those obtained in the
396 absence of salt. A further increase of MgCl_2 concentration at 0.5 M induces a small decrease in the
397 adsorption efficiency in agreement with the general behavior observed in the presence of
398 monovalent cation salt.

399 On the contrary of MgCl_2 , the effects produced by similar amounts of CaCl_2 in solution are more
400 pronounced. The system's adsorption efficiency decreases remarkably by increasing the
401 concentration of CaCl_2 from 0 to 0.1 M (**Figure 5B**). According to the behavior observed in the
402 case of NaCl, a further increase of CaCl_2 concentration causes a change of trend; the adsorption
403 efficiency increases instead of decreasing (**Figure 5B**).

404 The reason for such a relevant difference in the effect of these two salts containing both a divalent
405 cation could be ascribed to the different ways of Magnesium and Calcium to interact with water and
406 cyclodextrins. As reported by Nicolis et al. (1996), Ca^{2+} can be directly coordinated by three
407 hydroxyl groups of cyclodextrin through the lone-pairs of these OH groups' oxygen atoms (Nicolis
408 et al., 1996). The calcium/polymer interaction occurring in the outer part of CDs modifies the
409 general three-dimensional polymer structure and, consequently, CDs accessibility towards SMX. As
410 proof of these structural modifications, there is the post-synthetic treatment of β -EPI polymer with
411 Calcium Chloride solutions suggested in the literature to make a more rigid product, i.e., resulting

412 in less swollen in water (Moon et al., 2008). Also, the Mg^{2+} can interact with CD but, being
413 octahedrally coordinated by water molecules to form complex $[Mg(H_2O)_6]^{2+}$ cations, it forms
414 intermolecular bridges via aqua ligand molecules with CDs, which give rise to a less important
415 structural polymer change (Nicolis et al., 1995).

416

417

Figure 6

418

419 *3.7 Effect of size and charge of anions*

420 Further, in-batch SMX adsorption experiments were carried out using sodium bromide, sodium
421 perchlorate, and sodium sulfate at 0.1 M concentration to assess the influence of inorganic anions
422 on SMX adsorption onto the β -EPI polymer. As shown in **Figure 6**, the adsorption percentage
423 decreases dramatically with the increase in the monovalent anion size. In proximity to the
424 hydrophobic sites of the adsorbent, the water layering is energetically not very favorable. Therefore,
425 anions larger than the chloride, which are more polarizable, can establish hydrophobic interactions
426 with the polymer's apolar sites (Kunz, 2010) competing with SMX^- anions for adsorption. The
427 larger the anion size ($ClO_4^- > Br^- > Cl^-$), the higher the occupied area on the polymer and the more
428 hindered the attachment of SMX^- . In the case of Na_2SO_4 , the increased ionic strength of the
429 medium may cause a salting-out phenomenon, which would counterbalance the competitive effect
430 exerted by sulfate anions, thus providing an adsorption efficiency similar to that found in the
431 absence of salts.

432 *3.8 Desorption of SMX from β -EPI polymers and adsorbent recycling*

433 One of the most concerning problems is the disposal of adsorbent materials after their use since they
434 can become secondary pollution sources. Many research works showed the interesting possibility of
435 regenerate and reuse the cyclodextrin polymers after the adsorption of contaminants mainly through
436 organic solvent extraction, since most of the adsorbates have a hydrophobic nature (Morin-Crini et
437 al., 2018; Vito Rizzi et al., 2019; Romita et al., 2019). As described before, in the presence of

438 anions such as bromide and perchlorate, the adsorption of SMX onto the β -EPI results unfavored.
439 These conditions could be exploited for SMX release from the material. Therefore, in-batch SMX
440 desorption experiments were performed with sodium bromide aqueous solutions at 0.1, 0.5, and 1
441 M concentrations, room temperature, neutral pH, and using a contact time of 30 minutes. As
442 depicted in **Figure 6**, NaBr allowed an efficient recovery of SMX from the β -EPI adsorbent, which
443 can be attributed to the substitution of the pollutant molecules and ions with bromide ones. In
444 particular, the desorption efficiency was 67.7% with 0.1 M salt concentration; it increased at 95.1%
445 in the presence of 0.5 M NaBr and decreased at 90.5% using 1 M NaBr. Based on these results, 0.5
446 M was chosen as the optimum concentration of sodium bromide for SMX desorption experiments. 5
447 cycles of consecutive adsorption and desorption were conducted in the conditions already described
448 to verify the possibility of recycling β -EPI polymer multiple times.

449

450

Figure 7

451

452 As shown in **Figure 7**, the SMX desorption efficiency remained approximately constant for all 5
453 cycles, around 90%. Moreover, the adsorption ability of β -EPI increased by about 10% from the
454 third cycle onwards. Cycles of consecutive adsorption/desorption partially modify the swelled
455 polymer structure, as confirmed by comparing DSC thermograms of the polymer before the
456 adsorption and after the 1st and the 5th adsorption/desorption cycle. The broad endothermic peak,
457 associated with the water loss from the polymer, and the endothermic peak observed at a higher
458 temperature, associated with the fusion and beginning of the decomposition process, are shifted at a
459 higher and lower temperature, respectively when the polymer is subjected to subsequent
460 adsorption/desorption cycles. These differences suggest that the salt treatment, used to promote the
461 desorption, could induce a reorganization of the polymeric network that does not alter its adsorbent
462 capacity (**Figure S3**). Therefore, it can be asserted that β -EPI can be easily regenerated and reused
463 more than five times to remove SMX without losing performance.

464 **4. Conclusions**

465 This water-insoluble cyclodextrin-epichlorohydrin polymer, already tested as adsorbent for other pollutants,
466 can be used to remove also SMX from water. The overall results, indeed, indicate that β -EPI polymer
467 is not only capable of removing SMX by adsorption with short contact times and a $q_{\max} = 10$ mg/g
468 but it is also easily regenerated using a 0.5 M solution of sodium bromide without any loss in the
469 adsorption performance and with obvious both economic and environmental advantages. The cost-
470 effectiveness of this polymer, compared to other materials like activated carbons, together with its
471 adsorption capacity, large removal rate, wide spectrum of action, robustness and reusability makes
472 this material interesting for practical applications in waste water treatment.

473

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CAPTIONS

Figure 1. (a) Influence of the contact time on the adsorption capacity q_t (mg g^{-1}) of SMX onto β -EPI polymer (25 mg/mL) at different SMX concentrations : (■) 1.3 mg/L, (●) 5 mg/L, (▲) 10 mg/L and (▼) 15 mg/L; (b) dependence of the SMX maximum adsorption percentage on SMX concentration. (c) Influence of the β -EPI polymer dose at a constant SMX concentration (10 mg/L): (■) 3.13 mg/mL, (●) 6.3 mg/mL, (▲) 13 mg/mL and (▼) 25 mg/mL; (d) dependence of the SMX maximum adsorption percentage on β -EPI polymer dose. (e) Influence of the temperature at constant SMX concentration (10 mg/L) and β -EPI polymer dose (25 mg/mL): (■) 293 K, (●) 313 K and (▲) 333 K; (f) dependence of the SMX maximum adsorption percentage on temperature. (g) Influence of pH at constant SMX concentration (10 mg/L) and β -EPI polymer dose (25 mg/mL): (■) 2.0, (●) 4.5, (▲) 7.0, (▼) 9.5 and (◄) 12.0; (h) dependence of the SMX maximum adsorption percentage on pH.

Figure 2. Pseudo second order kinetic model (a) at SMX constant (10 mg/L) varying β -EPI polymer doses ((■) 3.13 mg/mL, (●) 6.3 mg/mL, (▲) 13 mg/mL and (▼) 25 mg/mL), (b) at β -EPI polymer dose constant (25 mg/mL β -EPI) varying SMX concentration ((■) 3.13 mg/mL, (●) 6.3 mg/mL, (▲) 13 mg/mL and (▼) 25 mg/mL)

Figure 3. Intraparticle diffusion model plots for SMX ((■) 5.0 mg/L, (●) 15 mg/L) adsorption onto β -EPI polymer (25 mg/mL)

Figure 4. Influence of NaCl concentration ((■) no salt, (●) 0.1 M, (▲) 0.5 M, (▼) 1.0 M and (◄) 1.5 M) on adsorption of SMX (10 mg/L) onto β -EPI polymer (25 mg/mL).

Figure 5. (a) Influence of MgCl_2 ((■) no salt, (●) 0.05 M, (▲) 0.1 M and (▼) 0.5 M) and CaCl_2 ((■) no salt, (●) 0.05 M, (▲) 0.1 M and (▼) 0.5 M) concentration on adsorption of SMX (10 mg/L) onto β -EPI polymer (25 mg/mL).

Figure 6: Effect of different salt 0.1 M on SMX (10 mg/L) adsorption onto β -EPI polymer (25 mg/mL).

Figure 7: Effect of different concentration of NaBr on the desorption of SMX (10 mg/L) (a) and efficiency of five consecutive adsorption/desorption cycles

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Table 1: Pseudo-second order kinetic parameters for adsorption of SMX onto the β -EPI polymer

25 mg/g of β -EPI polymer					10 mg/g of SMX				
SMX (mg/g)	q_e (exper)	q_e (calc)	k_2 (g mg ⁻¹ min ⁻¹)	R^2	β -EPI polymer (mg/g)	q_e (exper)	q_e (calc)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
1.3	0.024	0.024	80.343	0.991	3.13	0.826	0.871	1.099	0.959
5	0.104	0.104	28.850	0.993	6.3	0.676	0.663	0.409	0.969
10	0.246	0.248	6.631	0.992	12.5	0.389	0.375	3.979	0.994
15	0.430	0.407	4.660	0.977	25.0	0.246	0.248	6.631	0.992

Table 2: Thermodynamic parameters for the adsorption of SMX onto the β -EPI polymer

Temperature	K_{eq}	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
293	63.894	-10.127	-26.123	-56.188
313	25.932	-8.472		
333	10.618	-6.541		

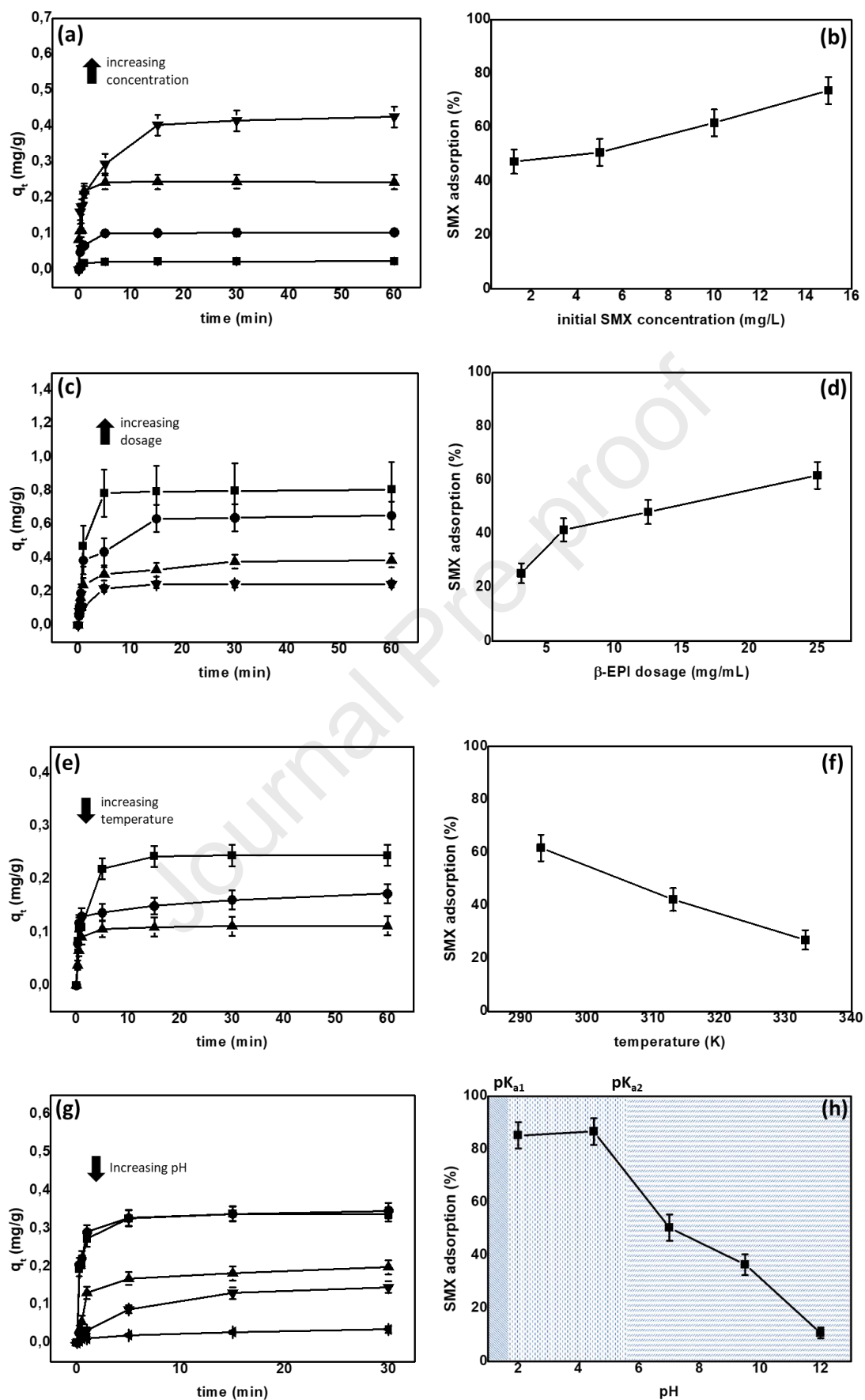


FIGURA 1

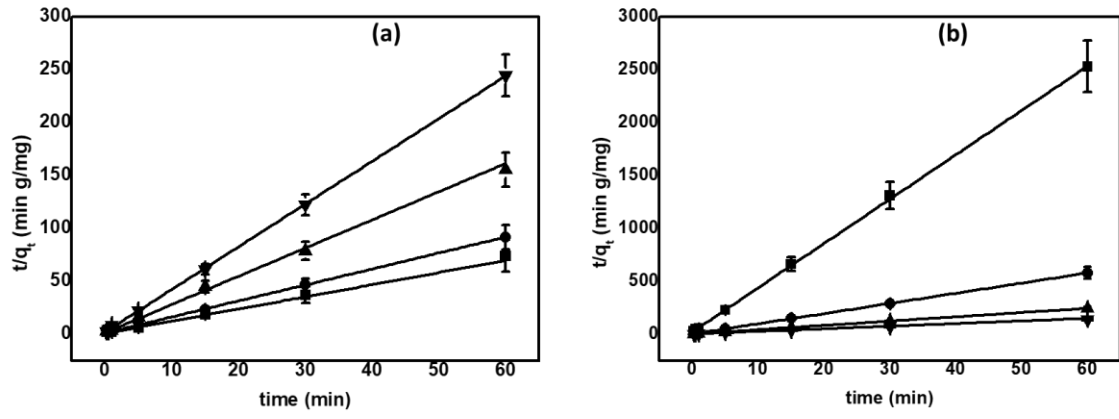


FIGURE 2

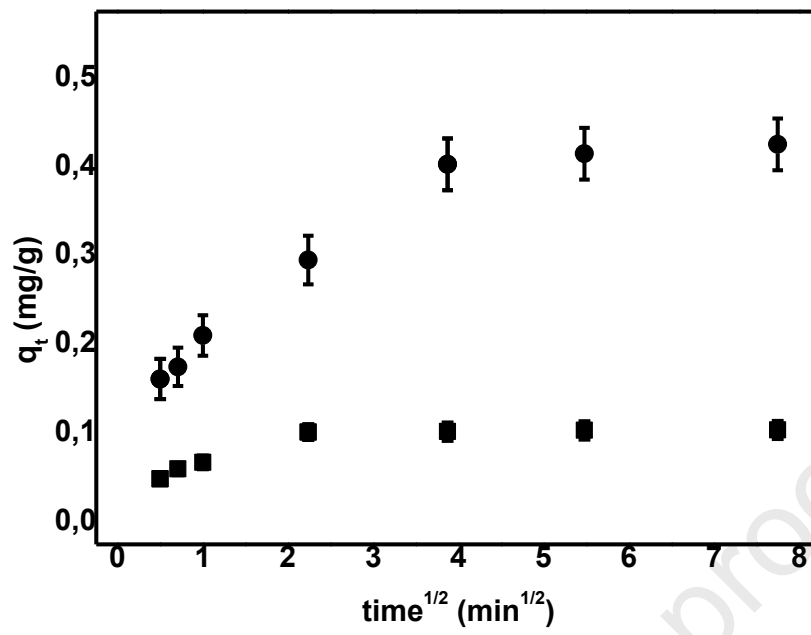


FIGURE 3

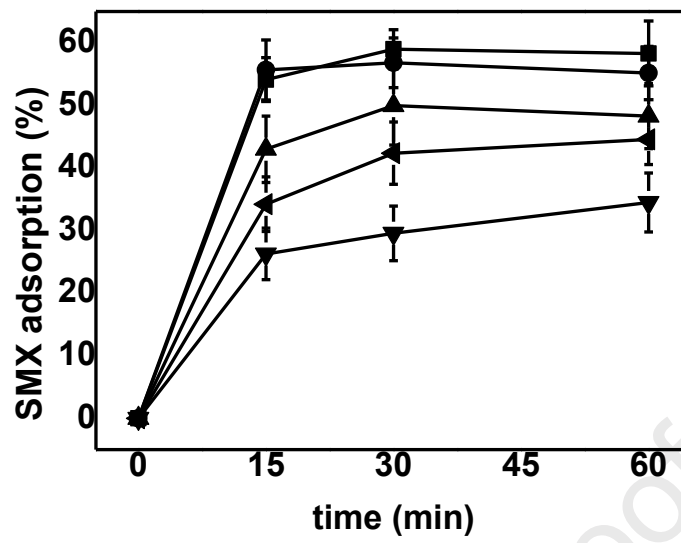


FIGURE 4

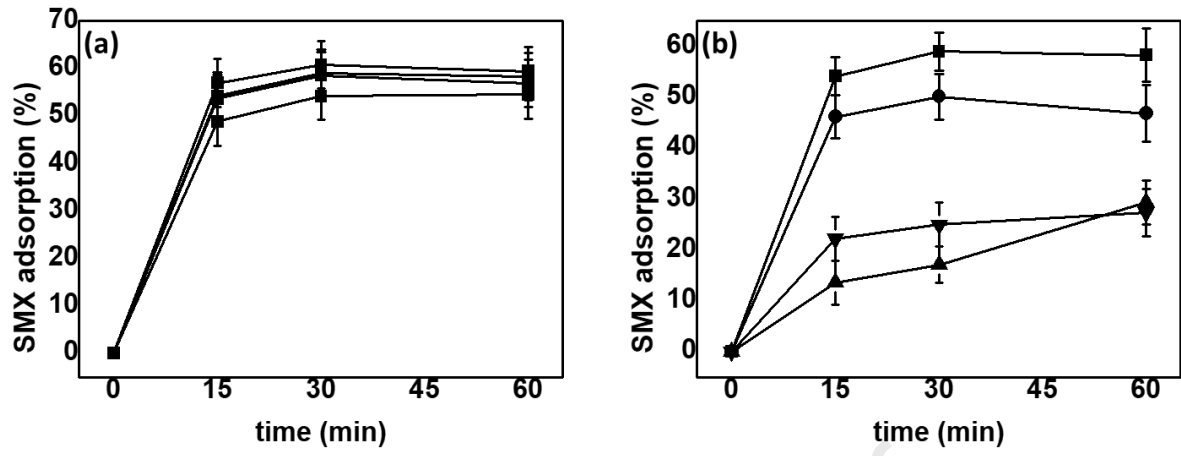


FIGURE 5

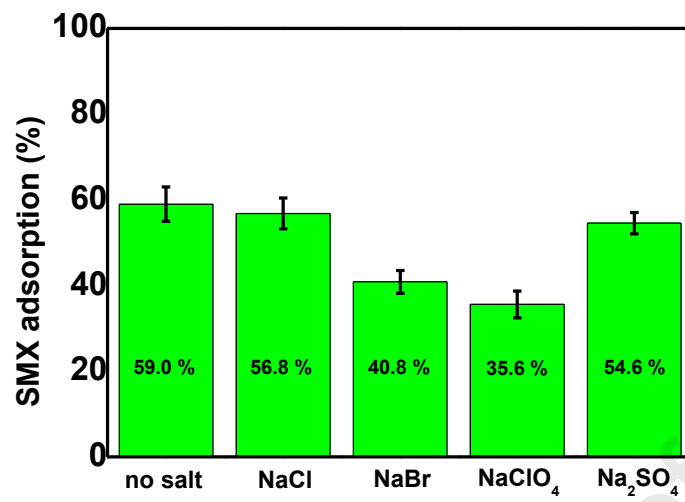


FIGURE 6

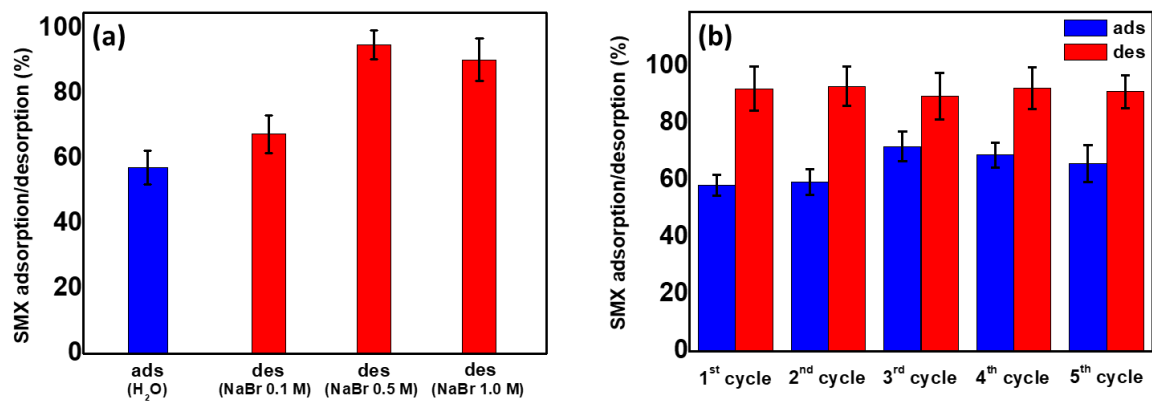


FIGURE 7

Highlights

- Quick removal of sulfamethoxazole from wastewater by adsorption.
- Validation of β -EPI polymer as adsorbent material for wastewater treatment plants.
- Regeneration of β -EPI polymer as adsorption material by a sustainable approach.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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