A review of the adsorption-biological hybrid processes for the abatement of emerging pollutants: removal efficiencies, physicochemical analysis, and economic evaluation

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Abstract

The limited efficiency of conventional wastewater treatment plants (WWTPs) in emerging pollutants (EPs) removal encourages the development of alternative technologies for the adequate treatment of wastewater, due to its adverse effects on human health and ecosystems. The biological, physical or chemical hybrid technologies to treat EPs results interesting since they can enhance the performance of WWTPs. Among them, hybrid adsorption/biological technology could offer different possibilities that are explored in this work (PAC-MBR, PACT/GAC-CAS, BAC configurations). In this way, different variations in the adsorption process have been considered: the form of the adsorbent, the feed to the system, and the type of biological process, either conventional activated sludge (CAS), membrane bioreactor (MBR) or biofilm systems. For each combination, the removal efficiency of micropollutants, classified according to their use into pharmaceuticals, personal care products (PCPs) and other micropollutants (mainly benzotriazoles) was analysed. From reported data, it was observed a beneficial synergistic effect of dipole moment and octanol–water partition coefficient on the removal efficiency of micropollutants by adsorption/biological hybrid technology. Finally, a preliminary economic evaluation of the powdered activated carbon in a conventional activated sludge

27 reactor (PACT), powdered activated carbon-membrane bioreactor (PAC-MBR) and

28 biological activated carbon (BAC) hybrid systems was carried out by analysing the capital

29 expenditure (CAPEX) of plants for capacities up to 75 000 m^3d^{-1}. Likewise, estimations

30 of adsorbent concentration for a hypothetical plant with a capacity of 10000 m^3d^{-1} is

31 presented. Among these hybrid configurations, PAC-MBR achieved the highest

32 micropollutant elimination percentages; however, it presents the highest CAPEX and

33 activated carbon requirements.

34

35 **Keywords**: micropollutants, physical-biological hybrid technologies, activated carbon,

36 activated sludge, membrane bioreactor, wastewater

37

1. INTRODUCTION

The rapid development of modern society produced during last decades has resulted in a considerable rise in human activities requiring the use of organic solvents (Gavrilescu et al., 2015). This has resulted in the discharge into the aquatic environment of a very extensive group of compounds, such as pharmaceuticals, drugs, personal care products (PCPs), steroids, hormones, surfactants, perfluorinated compounds (PFCs), flame retardants, industrial additives, as well as their transformation products (TPs) (Farré et al., 2008). Furthermore, their persistence in the environment and the adverse effects on human health and ecosystems are some of their more remarkable characteristics. In fact, in the 2004-2018 period, 27-31% of the total chemicals production were environmentally hazardous substances and, in 2018, over 74% of these chemicals were hazardous to the health (Eurostat, 2019). Moreover, the presence of small concentrations of these micropollutants in water (ranging from ng L^{-1} to µg L^{-1} (Luo et al., 2014)), called emerging pollutants (EPs), has been linked to chronic toxicity, endocrine disruption and the development of pathogen resistance (Rosal et al., 2010). In this context, the European Union Water Framework Directive 2000/60/EC reported a list of 33 priority substances, and every two years, Watch Lists include new compounds (Commision, 2018). Anyway, there are still scarce legislation related to emerging pollutants.

Conventional wastewater treatment plants (WWTPs) were not designed for the removal of micropollutants (Mailler et al., 2015). For this reason, most hydrophilic and refractory micropollutants are not eliminated from wastewater (Mailler et al., 2015; Mailler et al., 2016). So, Gallé et al. (2019) reported null carbamazepine and lidocaine removal for in 18 WWTPs. Tang et al. (2019) observed similar results in the elimination of gemfibrozil, mefenamic acid, tolfenamic acid and diclofenac in two WWTPs from South China.

62 Several biological, physical and chemical processes have been evaluated to remove EPs

63 from wastewater. Activated sludge is one of the most usual biological treatments in

64 WWTPs, due to its low cost in comparison with other no biological technologies, like

65 chemical advanced oxidation processes, or its mild operation conditions (Wang and

66 Wang, 2016). However, this technique results to be ineffective when the emerging

67 pollutant is either recalcitrant to biodegradation, toxic to microorganisms or not easily

68 adsorbed onto suspended solids (Stott, 2003). Among the different chemical techniques,

69 advanced oxidation processes (AOPs) have been significantly studied for the removal of

70 emerging pollutants. However, AOPs have some disadvantages: high energy

71 requirements, high operational and maintenance cost (Dhangar and Kumar, 2020; Taoufik

72 et al., 2020), as well as the formation of toxic or persistent by-products during the

73 oxidation process (Gerrity et al., 2011; Akhtar et al., 2016). Finally, among physical

74 techniques, membrane filtration and adsorption by activated carbon are the most

75 attractive. Nevertheless, nanofiltration and reverse osmosis are still partially permeable

76 to some trace organic contaminants and present high operation costs (Steinle-Darling et

77 al., 2010; Grassi et al., 2013; Luo et al., 2014).

78 On the other hand, adsorption has been widely applied as treatment to remove organic

79 compounds and synthetic chemicals (Ahmed et al., 2015; Akhtar et al., 2016). It achieved

80 removal percentages above 90% for pollutants such as sulfamethoxazole, bezafibrate,

81 ibuprofen, diclofenac, naproxen, carbamazepine and primidone (Wang and Wang, 2016).

82 Moreover, adsorption operation has a simpler design and softer operation conditions than

83 AOPs and membrane processes, and no toxic by-products are formed (Grassi et al., 2013;

84 Pi et al., 2018). However, the adsorbent must be accurately selected to guarantee an

85 adequate operation, being activated carbon the most common due to its high porosity and

86 specific surface area (Akhtar et al., 2016; Rodriguez-Narvaez et al., 2017). However, the

87   percentage of efficiency at pilot scale is far from expected: Meinel et al. (2014) reported

88   adsorption capacity at lab-scale almost ten times higher than at pilot scale (from 254 to

89   27 $\mu g \ g^{-1}$ in the case of carbamazepine).

90   Several authors studied activated carbon adsorption as advanced technology after

91   biological treatments of WWTPs and they observed significant improvements in the

92   elimination of some recalcitrant micropollutants (Boehler et al., 2012; Margot et al., 2013;

93   Mailler et al., 2014; Mailler et al., 2016; Guillossou et al., 2019). However, Guillossou et

94   al. (2019) obtained removal percentages below 80% in the elimination of some emerging

95   pollutants, like carbamazepine. This low performance could be enhanced by increasing

96   the dosage of activated carbon or by combining adsorption with another technology, like

97   biological treatment.

98   With these antecedents, the combination of some of the aforementioned technologies to

99   create hybrid techniques could be an effective and economical option (Scott and Ollis,

100   1995; Rodriguez-Narvaez et al., 2017). Alternatives such as the combination of

101   adsorption and biological techniques have been widely applied for phenolic substances

102   (Meidl, 1997; Lin and Juang, 2009) and some hybrid technologies, such as biological

103   activated carbon (BAC) filtration systems, have started to be adopted to treat emerging

104   pollutants in water and wastewater (Thuptimdang et al., 2020). As result, it has been

105   shown that they could be more efficient that single treatments (Boehler et al., 2012;

106   Dhangar and Kumar, 2020). In this way, several benefits were observed for integration

107   of adsorption on activated carbon and biological treatments: (a) improvement of its

108   bioactivity, since the activated carbon adsorbs inhibitory or toxic compounds for the

109   biomass (Sublette et al., 1982); (b) hindering of membrane biofouling in membrane

110   bioreactors (Çeçen and Aktas, 2011); (c) lower operation cost than separate biological

111   and physicochemical systems (Çeçen and Aktas, 2011; Jafarinejad, 2017b; Boehler et al.,

112 2012; Margot et al., 2013)); and, (d) enhanced sludge management, since the activated

113 carbon increases the solids content (50% of solids in sludge with activated carbon versus

114 below 20% in a conventional sludge) (Sublette et al., 1982; Meidl, 1997). Furthermore,

115 the activated carbon can be regenerated through wet air oxidation (Meidl, 1997).

116 Although many scientific and review papers focus on the removal of EPs by chemical,

117 physical or biological technologies (Liu et al., 2009; Rivera-Utrilla et al., 2013; Wang

118 and Wang, 2016; Rodriguez-Narvaez, 2017; Arous et al., 2019), a very limited number

119 of articles deals with hybrid technologies. (Çeçen and Aktas, 2011, Grandclément et al.,

120 2017, Dhangar and Kumar, 2020). In particular, no work addresses comparison of hybrid

121 adsorption/biological process technologies for EP removal, as well as the influence of EP

122 properties on removal efficiency.

123   Thus, the scope of this work is to review the performance of the different adsorption/

124 biological hybrid processes for the EP removal: powdered activated carbon- membrane

125 bioreactor system (PAC-MBR), Powdered activated carbon treatment /Granular activated

126 carbon-conventional activated sludge system (PACT/GAC-CAS) and Biofilm or

127 biological activated carbon (BAC). To achieve this objective, data have been collected

128 from a total of 13 papers dealing with hybrid adsorption/biological processes for the

129 treatment of real or synthetic water both at lab and pilot scale. Only information about

130 pharmaceuticals, PCPs or benzotriazoles groups of emerging pollutants were observed.

131 In this way, among pharmaceutical compounds, antibiotics, anticonvulsants,

132 antidepressants, antihistamine, betablocker drug, hormones, iodinated x- ray contrast

133 media, lipid regulator, and anti-inflammatory drugs were considered. Concerning

134 personal care products (PCPs), musk fragrances, UV filters, anticorrosive agents, and

135 impurities of fluoroquinolones antibiotics were enumerated. Finally, a preliminary

136 economical evaluation of these technologies was carried out.

2. PHYSICAL PROPERTIES OF THE EMERGING POLLUTANTS

Table 1 summarized the main physical properties of emerging pollutants removed by adsorption, compounds that will be considered in the subsequent analysis (Additional emerging pollutant properties are included in Table S.1.). In this way, the solid-water distribution coefficient (K_d) provides an idea of the easiness of the pollutant to be adsorbed on the sludge: K_d values below 0.5 L gMLSS^{-1} mean negligible adsorption (Ternes et al., 2004). Similarly, Çeçen and Aktas (2011) fixed the low affinity to the sludge in $K_d < 0.3$ L gSS^{-1}. The logarithm of the octanol-water distribution coefficient (log K_{ow}), meanwhile, refers to the hydrophobicity of the substance and, therefore, its trend to be adsorbed on the activated carbon (Çeçen and Aktas, 2011). Van Beelen (2007) reported ranges of low (log $K_{ow} < 2.5$), medium ($2.5 < $ log $K_{ow} < 4$), and high (log $K_{ow} > 4$) adsorption on activated carbon trend. The biodegradation rate constant (K_{biol}) estimates the easiness of the compound to be biodegraded by the sludge. The emerging pollutant biodegradation rate has been considered as a pseudo first order (very low concentration of the pollutant, (Joss et al., 2006)) or a first order rate (the sludge concentration is constant at steady-state conditions (Fatta-Kassinos et al., 2010)). Joss et al. (2006) calculated the degradation rate as a pseudo first order and considered a hardly biodegradable ($K_{bio} < 0.1$ L g MLSS^{-1} day^{-1}), a biodegradable (0.1 L g MLSS^{-1} day^{-1} < $K_{bio} < 10$ L g MLSS^{-1} day^{-1}) and a highly biodegradable ($K_{bio} > 10$ L g MLSS^{-1} day^{-1}) substance. In this way, from these parameters, it is possible to identify the main emerging pollutants removal route among different elimination pathways: adsorption onto the activated carbon, adsorption onto the sewage sludge and biodegradation of the biomass. Specifically, the EP property which presents the highest value, will represent the main removal route.

3. ADSORPTION / BIOLOGICAL DEGRADATION HYBRID CONFIGURATIONS

The hybrid technology tries to integrate the advantages of both techniques, being the adsorption incorporated in the biological treatment. In this section, the available hybrid adsorption-biological treatments for wastewater treatment are described.

Variations in the adsorption process are accomplished by either changes in the adsorbent shape/size or the feed system. The activated carbon can be used as either powdered activated carbon (PAC) or granular activated carbon (GAC). Concerning the feed system, the adsorbent could be contained in the media as microorganisms carrier, as suspended solid or it can be continuously fed, either as dry particles or as adsorbent slurry. Concerning the biological process, either conventional activated sludge (CAS), membrane bioreactor (MBR) or biofilm systems are proposed for these processes.

Combining the aforementioned aspects, the main hybrid technologies to be reviewed are: powdered activated carbon in a conventional activated sludge reactor (PACT), granular activated carbon in a conventional activated sludge reactor (GAC-CAS), powdered activated carbon in a membrane bioreactor (PAC-MBR), and granular activated carbon in a biofilm reactor (BAC). An operation scheme of these technologies is shown in figure 1.

3.1. PACT and GAC-CAS technologies

Hybrid technologies which include a conventional activated sludge (CAS) bioreactor could differ in the shape of the activated carbon: powered, PACT, or, granular, GAC-CAS, being the first one the most used. A PACT configuration consists of the addition of PAC within the aeration tank or in the sludge recycling line of a CAS system. The adsorption equilibrium is ensured since sludge retention time (SRT) is in the range 10-50

185   days (Çeçen and Aktas, 2011). Additionally, PAC can leave the system with the waste

186   sludge or it can be partially recirculated with the activated sludge (Boehler et al., 2012).

187   PAC concentration is kept by a continuous dosage of the fresh or regenerated adsorbent

188   in the biological reactor. Concerning the carbon dose, Obrecht et al. (2015) reported

189   dosages from 10 to 18 mg L^{-1} in PACT to treat flowrates from 31 to 11640 $m^3 d^{-1}$ of urban

190   wastewater, reaching elimination percentages of at least of 80% for micropollutants such

191   as benzotriazol, carbamazepin, diclofenac, mecoprop or sulfamethoxazol (Lema and

192   Suarez, 2017). The COD, N-NH$_4$ and P-PO$_4^{-3}$ concentrations of the influent were 334,

193   30 and 5 mg L^{-1}, respectively (Obrecht et al., 2015). The PAC is separated in the

194   secondary settler, where a small dose of cationic polyelectrolyte can be added (Çeçen and

195   Aktas, 2011).

196   Additionally, the PAC can be replaced by GAC in a sequential batch reactor (SBR) or in

197   the aeration tank of a CAS process, being SBR more used. (Sirianuntapiboon, 2002;

198   Sirianuntapiboon and Sansak, 2008). However, a larger volume of activated carbon is

199   required for the granular than the powdered adsorbent, with values of 1000 mg L^{-1} versus

200   30 mg L^{-1} to achieve carbamazepine elimination percentages of 43 and above 90%,

201   respectively (Serrano et al., 2010; Boehler et al., 2012).

202   Concerning the estimated cost, PACT technology is reported as the most profitable

203   (Jafarinejad, 2017a). The PACT process only requires one-third of the capital cost, since

204   only two-thirds of a conventional activated sludge reactor is required to treat the same

205   volume of wastewater and one-eight of the operating cost of a conventional activated

206   sludge followed by granular activated carbon treatment (Jafarinejad, 2017a).

207   Furthermore, Meidl (1997) indicated 10% less in capital cost and 7% less of operating

208   cost per cubic meter of treated petrochemical wastewater when PACT configuration was

209   used instead of CAS (operating costs of 0.98 $ m^{-3} versus 1.05 $ m^{-3}) (Jafarinejad, 2017a).

3.2.   PAC-MBR technology

The presence of powdered activated carbon in an MBR reactor improves the emerging pollutants removal up to 10-80%, and in the case of highly biodegradable micropollutants up to 80-100% (Baumgarten et al., 2007; Li et al., 2011; Serrano et al., 2011; Alvarino et al., 2017). The activated carbon also mitigates membrane biofouling in the biorreactor since the extracellular polymeric substances (EPS), where microorganisms are embedded, present higher affinity towards the activated carbon, avoiding accumulation on the membrane surface (Çeçen and Aktas, 2011; Jia et al., 2014). The activated carbon is added in the MBR or in the aerobic tank previous to the membrane chamber, either as hydrated slurry (Westerhoff et al., 2005), or as a pulse during the membrane backwashing (Campos et al., 2000). The concentration varies between 15 and 4000 mg L^{-1} (Lesage et al., 2008; Li et al., 2011; Serrano et al., 2011; Hu et al., 2017; Echevarría et al., 2019).

These bioreactors can be sequentially (PAC-sMBR) or not sequentially (PAC-MBR) operated. In the first case, the MBR works at intervals of less than 6 h divided into cycles of filling, anoxic/aerobic reaction, settling and effluent withdrawal (Serrano et al., 2011). In both cases, membrane cleaning periods are required: 5-7.5 min of membrane suction followed by 0.5-5 min of membrane backwashing (Lesage et al., 2008; Li et al., 2011; Serrano et al., 2011; Alvarino et al., 2017; Hu et al., 2017).

Regarding the estimation cost of PAC-MBR, Shoener et al. (2016) compared it to CAS. As a results, it was observed a total cost saving of 25%, and a net energy consumption reduction from 0.3/0.6 kWh m^{-3} to -0,09/-0.06 kWh m^{-3} (energy positive performance). However, Remy et al. (2009) pointed out that, although PAC reduces membrane fouling, it increases the cost of the plant. In this sense, for low PAC addition (0.5 g L^{-1}) and high SRT value (50 days), the lowest additional cost is 0.008 € / m^3 of wastewater.

3.3. BAC technology

The BAC technology is usually applied as tertiary treatment. It consists of the GAC addition in a biofilm reactor to act as the biofilm support media where microorganisms are attached by forming biological activated carbon. According to Pirbazari et al. (1990), this biofilm configuration supports more biomass than other solid media as synthetic carbonaceous adsorbents or sand. For example, Knezev (2015) reported concentrations of 10^9-$4 \cdot 10^{10}$ and $3 \cdot 10^7$-$2 \cdot 10^{10}$ cells per cm^3 in GAC and sand filters, respectively. BAC technology achieved EP removal above 80%, working with a contact time of 17 minutes and 100 days of operation (Paredes et al., 2016). Generally, at laboratory and pilot scale, the bioreactor column is previously packed with a GAC dosage between 15-73 g in reactor volumes from 0.024 to 0.245 L (Song et al., 2006; Aslam and Kim, 2019) and between 500-1820 g in reactor volumes among 10-11 L (Khodadoust et al., 1997; Wilson et al., 1998; Kim and Logan, 2000). Then, the activated sludge is seeded and acclimated for 5 days (Song et al., 2006) for the biofilm formation in the adsorbent media (Khodadoust et al., 1997; Kim and Logan, 2000). Optionally, at large pilot scale, the GAC can be continuously added in the previously seeded biorreactor until concentrations of 300 g L^{-1} (Mailler et al., 2016). Likewise, periodic GAC replacement is advisable: Khodadoust et al. (1997) added 2.5-5 g d^{-1} of fresh GAC after 286 days of operation.

The treated wastewater down-flow operation has been widely proposed (Khodadoust et al., 1997; Wilson et al., 1998; Wang and Chang, 1999; Kim and Logan, 2000; Mailler et al., 2016) since lower fluid velocities are required; minimum fluidization velocity of 2.3 m h^{-1} in down-flow operation (Garcia-Calderon et al., 1998; Song et al., 2006) versus 21 m h^{-1} in up-flow (Wang and Chang, 1999). Furthermore, the biofilm bed can be fixed or moved, depending on the inlet flowrate. In this way, different kinds of BAC systems are possible. The fluidized-bed reactor is an integrated activated carbon/biological

259 configuration highly used when a GAC is selected (Çeçen and Aktas, 2011). Generally,

260 the activated carbon is expanded in the 25-30% of the bioreactor total volume (Pfeffer

261 and Suidan, 1989; Khodadoust et al., 1997).

262 Expanded or fluidized-bed BAC reactors present many benefits over the fixed-bed BAC

263 system, such as minimizing fouling problems, higher removal efficiencies and higher

264 operation capacity. However, operating costs increase due to fluidization of the bed

265 (Çeçen and Aktas, 2011).

266

267 **4. REMOVAL OF EMERGING POLLUTANTS BY ADSORPTION /**

268 **BIOLOGICAL DEGRADATION HYBRID CONFIGURATIONS**

269 For comprehensive reading, discussion on the emerging pollutants removal is grouped by

270 type (pharmaceuticals, personal care products (PCPs) and other micropollutants) and

271 applied technology.

272 Table 2 summarized the emerging pollutants removal achieved by different

273 configurations, considering the average efficiency obtained from literature. Likewise,

274 Table S.2 (Supplementary Material) detail specific characteristics of the process

275 involving the activated carbon of Table 2. In this way, activated carbon is introduced in

276 the reactors until final concentration from 15 to 1000 mg L^{-1}. The initial EPs concentration

277 treated in the technologies were in all cases below 50 μg L^{-1}, excepting from Li et al.

278 (2011) who work with EP initial concentrations of 750 μg L^{-1} (Table S.2). Performances

279 reported in the literature, as well as the main operation conditions, water quality achieved,

280 system volume and operational time, are summarized in Table 3.

281 Most of the works deal with synthetic or real municipal wastewater, and only Echevarría

282 et al., (2019) and Alvarino et al., (2018) treated wastewater from a reclamation plant and

283 from an hospital, respectively. Likewise, the purification objectives set by the directive

284 (91/271/EEC) are mostly achieved in the analysed works. COD and N-NH$_4$ removal

285 efficiencies are above 85 and 70 %, respectively, with COD, and N-NH$_4$ effluent

286 concentrations of 4-68 mg COD L^{-1} and 0.2-16 mg N-NH$_4$ L^{-1}. However, Alvarino et al.

287 (2016) and Alvarino et al. (2018) found encountered some difficulties in decreasing levels

288 of P-PO$_4^{-3}$. In these works, a wide range of biomass concentration (32-10100 mg VSS L^{-}

289 ^{1}) and temperature (8-25 ºC) has been used -in this case justified because the studies were

290 carried out in different seasonal periods, from 92 to 974 days -. In the case of pH, the

291 interval ranged from 6 to 8.9.

4.1. Removal of pharmaceuticals

4.1.1. Application of PACT/GAC-CAS reactors

294 Elimination of several antibiotics, anticonvulsants, antidepressants, iodinated x-ray

295 contrast media, anti-inflammatory drugs and other pharmaceuticals (such as an

296 antihistamine, a betablocker drug and a lipid regulator) were studied in PACT and

297 GAC- CAS configurations.

298 Boehler et al. (2012) tested the removal of two antibiotics, clarithromycin (CAM) and

299 sulfamethoxazole (SMX), in a PACT system, with a final concentration of activated

300 carbon between 15 and 30 mg L^{-1}. Clarithromycin removal varied from 50-60% up to

301 above 95% and 99% after PAC addition at the lowest and largest concentration,

302 respectively. Furthermore, the improvement percentages (obtained dividing the

303 difference of removal percentages with and without activated carbon by the removal

304 percentage without activated carbon) were 42 and 44% for both PAC concentrations (15

305 and 30 mg L^{-1} of PAC, respectively). For identical activated carbon concentration, the

306 SMX elimination varied from 10-20% in a CAS reactor, up to among 20-30% and 30-

307 40%, after the addition of PAC until final concentrations of 15 and 30 mg L^{-1},

308 respectively (improvement percentages of 40 and 57 % with the lowest and highest

309 concentration of PAC, respectively).

310 CAM elimination is more favourable than SMX, in agreement with the higher values of

311 K_d and log K_{ow} for clarithromycin (0.26-1.2 L g MLSS^{-1} and 3.16, respectively) than for

312 sulfamethoxazole (0.011-0.5 L g MLSS^{-1} and 0.89, respectively). Furthermore, the

313 adsorption on activated sludge seems to be the main degradation way (versus

314 biodegradation), since both compounds exhibit very low biodegradation rate coefficients

315 (values below 0.5 and 7.6 L g MLSS^{-1} d^{-1}, for CAM and SMX, respectively), Table 1.

316 Boehler et al. (2012) also studied the removal of anticonvulsants, primidone (PR) and

317 carbamazepine (CBZ), in a hybrid PACT configuration with PAC concentrations between

318 15 and 30 mg L^{-1}. Primidone is scarcely degraded in the conventional activated sludge

319 process, achieving eliminations of 20-30% and 60-75% in a PACT configuration for PAC

320 concentration of 15 and 30 mg L^{-1}, respectively. Thus, sorption onto activated carbon is

321 the main removal pathway. In agreement, Pomiès et al. (2013) reported K_d (0.03-0.11 L

322 g MLSS^{-1}) and K_{biol} (0.0022- 0.1 L g MLSS^{-1} day^{-1}) coefficients compatible with

323 absence of adsorption onto sludge and biodegradation (K_d and K_{biol} below 0.3 L g MLSS^{-1}

324 ^{1} (Ternes et al., 2004) and 0.1 L g MLSS^{-1} day^{-1} (Joss et al., 2006), respectively). The

325 log K_{ow} coefficient, 1.12 (Table 1), is compatible with preferent adsorption on the

326 activated carbon.

327 Similar conditions were used by Boehler et al. (2012) in the carbamazepine elimination,

328 and degradation moved from 20% to 90-95% after PAC addition. Moreover, Serrano et

329 al. (2010) just obtained 43% removal of the anticonvulsant in a GAC-CAS configuration

330   with 1000 mg L^{-1} of activated carbon. These results indicate that, in a CAS reactor, the

331   use of PAC is more effective for the removal of carbamazepine than the use of GAC.

332   Finally, by observing the removal percentages of these anticonvulsants when a CAS is

333   used, it can be concluded that carbamazepine (CBZ) is a more easily eliminated than

334   primidone (PR). This can be attributed to the higher log Kow values of carbamazepine

335   (between 2.3-2.5) than primidone (1.12).

336   Regarding the benzodiazepine group of antidepressants, three compounds were studied:

337   diazepam (DZP), oxazepam (OXA) and venlafaxine (VEN). Serrano et al. (2010)

338   investigated DZP in a GAG-CAS configuration and the removal percentage changed from

339   10-25% up to 32% when the reactor had a GAC final concentration of 1000 mg L^{-1}.

340   Elimination of OXA was only studied by Boehler et al. (2012) in a PACT configuration,

341   achieving percentages from null to 80-95% when PAC was added until a final

342   concentration of 30 mg L^{-1}.

343   VEN was analysed in a PACT configuration by Boehler et al. (2012) and the addition of

344   PAC until final concentrations of 15 and 30 mg L^{-1} resulted in similar modifications of

345   the removal percentage from 10-20% to 90-95%. The main removal route of VEN is

346   sorption onto activated carbon, whereas biodegradation and adsorption on activated

347   sludge are negligible. In agreement, this substance presents low values of K_d and K_{biol}

348   and high hydrophobicity (log Kow of 3.4), Table 1.

349   In general, venlafaxine (VEN) is the most easily removed compound through activated

350   carbon adsorption followed by oxazepam (OXA) and diazepam (DZP). These results are

351   in agreement with their log Kow coefficients. Regarding the use of PAC or GAC in the

352   system, the powdered adsorbent performance is the most favourable. Finally, the removal

353   percentages in absence of the adsorbent for all the antidepressants resulted very low since

354   all compounds presented low values of K_d and K_{biol} coefficients (Table 1) indicating that

355   adsorption onto activated carbon is the main removal pathway.

356   Regarding the iodinated x-ray contrast media group of pharmaceuticals, Boehler et al.

357   (2012) studied iohexol (IOH) and iopromide (IOP) in PACT configuration. For IOH,

358   elimination percentages changed from 0-10% to 40% or 80% when a concentration of 15

359   or 30 mg L^{-1} of PAC were added, respectively. In the case of IOP, removal percentages

360   changed from 40% to 55-60 or 80-90%, in absence or presence of the different PAC

361   concentrations. From these results, it can be observed that IOP is a more biodegradable

362   substance than IOH since it presents a lower K_{biol} value.

363   Three anti-inflammatory pharmaceuticals, diclofenac (DCF), ibuprofen (IBP) and

364   naproxen (NPX), were studied in PACT and GAC-CAS technologies, whereas

365   mefenamic acid (MFA) and codeine (COE) were only analysed in PACT configurations.

366   Specifically, Boehler et al. (2012) studied MFA, COE, DCF, IBP and NPX in a CAS

367   reactor where PAC was added until final concentrations of 15 and 30 mg L^{-1} in the

368   aeration tank. As a result, the removal percentages improved independently of the PAC

369   dosage for MFA (from 80-90% to 90-95%) and IBP (from above 80% to above 95%) but

370   not for the other anti-inflammatory drugs. DCF was removed from 0-10% to 60-75% or

371   80-95%, when PAC was added until final concentrations of 15 and 30 mg L^{-1},

372   respectively. Similarly, COE changed from 20-25% to 80% or 88%, and NPX from above

373   70% to 75-80% or 90-95% for the increasing PAC concentrations.

374   Serrano et al. (2010) analysed the removal of DCF, IBP and NPX in a GAC-CAS

375   configuration with 500 mg L^{-1} of GAC in the biological system. Although the presence

376   of GAC enhanced the elimination percentages of DCF (from 74% to 85%), any

377   improvement was observed for IBP and NPX, where the removal percentages were kept

378 in 85-99 % and above 90 %, respectively. Furthermore, it can be observed that the

379 elimination percentages obtained in the biological system were quite similar to the results

380 observed by Boehler et al. (2012). This can be explained since, although the SRT in the

381 bioreactor was considerably higher than used by Serrano et al. (2010) (2-4 days versus 1

382 day), the concentration of mixed liquor suspended solids (MLSS) was lower (400 mg

383 MLSS L^{-1} versus 4160 mg MLSS L^{-1}).

384 Finally, Boehler et al. (2012) studied the elimination of an antihistamine (ranitidine), a

385 betablocker drug (atenolol) and a lipid regulator (bezafibrate) in a PACT configuration

386 with PAC concentrations of 15 and 30 mg L^{-1}. As a result, it was observed that the

387 presence of activated carbon considerably enhances the removal efficiency of these

388 pharmaceuticals. However, an increase in the adsorbent dosage does not ensure an

389 elimination improvement. In this way, the elimination percentage for bezafibrate changed

390 from 70-80% in absence of PAC to about 90 % in presence of PAC, respectively.

391 The elimination obtained for bezafibrate without PAC suggests that the main removal

392 route is biodegradation, (K_{biol} between 0.77-3 L g $MLSS^{-1}$ day^{-1}). Likewise, adsorption

393 onto activated carbon is also appreciable, due to the improvement of the elimination of

394 bezafibrate after PAC addition and its high log K_{ow} coefficient (Table 1).

395 As far as ranitidine (RAN) and atenolol (ATN) are concerned, adsorption onto activated

396 carbon is the main degradation pathway since its removal percentages changed from 48

397 to 99 %, for RAN, and from 40 to 95 %, for ATN, when activated carbon was added. In

398 this way, Khan and Ongerth (2004) also observed poor RAN and ATN elimination (23%

399 and 55%, respectively) in a WWTP where activated sludge was used as secondary

400 treatment.

4.1.2.   Application of PAC-MBR reactor

The following sections deal with the removal of several antibiotics, antidepressants, anti-inflammatory drugs, hormones and other pharmaceuticals (anticonvulsants, hormones and a betablocker drug) through the application of the PAC-MBR technology.

4.1.2.1. Removal of antibiotics

Baumgarten et al. (2007) analysed the removal of quinolone antibiotics -ciprofloxacin, enrofloxacin and moxifloxacin- with a hybrid PAC-MBR technology, at PAC concentration in MBR below 50 mg L^{-1} and among 50- 200 mg L^{-1}. For the highest PAC concentration (50-200 mg L^{-1} range), the removal efficiency of ciprofloxacin, enrofloxacin and moxifloxacin improved from 73, 56 and 78% up to above the 99% in all cases. Similarly, Alexandrino et al. (2017) reported elimination percentages of enrofloxacin from 40 to 55% when a constructed wetland was used as biological reactor to treat livestock wastewater. The close degradation percentages of ciprofloxacin and moxifloxacin (73 and 78%, respectively) are justified by the similar biodegradation coefficients of both pollutants: Dorival-García et al. (2013) reported for moxifloxacin a first order biodegradation coefficient between 0.0051- 0.0096 h^{-1}, and 0.0062-0.013 h^{-1} for ciprofloxacin. In agreement, the ciprofloxacin pseudo first order (0.55 L g $MLSS^{-1}$ day^{-1}), Table 1, confirms its biodegradability.

The improvement in the performance of the PAC-MBR hybrid technology against MBR is remarkable, although the log Kow of the three compounds is less than 2.5 (value below which the elimination by adsorption on activated carbon can be insignificant), Table 1. At this point, Baumgarten et al. (2007) and Dorival-García et al. (2013) identified adsorption of quinolone antibiotics onto activated sludge as the main removal via, followed by biodegradation. In agreement, the K_d value of ciprofloxacin is considerably high (20 L g $MLSS^{-1}$), Table 1. Therefore, the synergic effect of PAC-MBR could be

426   explained from the removal of toxic or inhibitory compounds for the biomass, by

427   adsorption on the PAC (Çeçen and Aktas, 2011; Jia et al., 2014).

428   Serrano et al. (2011) worked on the elimination of macrolide antibiotics, erythromycin

429   (ERY) and roxithromycin (ROX), in a sequential membrane bioreactor (PAC-sMBR)

430   with PAC concentration until 1000 mg L^{-1}. From comparison of PAC-sMBR technology

431   for both compounds, removal increments from 42-64% to 97- 99% for erythromycin, and

432   from 71-86% to 97-99% for roxithromycin, are observed. The greatest degradation of

433   roxithromycin in absence of activated carbon can be attributed to its higher

434   biodegradation rate coefficient (below 9 L gSS^{-1} d^{-1} for roxithromycin, and below 0.6 L

435   gSS^{-1} d^{-1} for erythromycin), Table 1. Furthermore, activated carbon increases the

436   efficiency of the process: 46% for erythromycin, and 20% for roxythromycin. Alvarino

437   et al. (2017) studied the removal efficiency of these two emerging pollutants (ERY and

438   ROX) in the same configuration and the addition of PAC enhanced the removal

439   percentage from 80 up to above 98%, in both cases, reaching improvements percentages

440   of 18%. Differences can be attributed to the membrane operation parameters: in the first

441   case, the mixed liquor volatile suspended solids (MLVSS) concentration varied from

442   3500 to 6000 mgMLVSS L^{-1} during 288 days, whereas, in the second case, MLVSS

443   ranged from 4800 to 8000 mgMLVSS L^{-1} during the 226 days. Thus, increasing MLVSS

444   concentration leads to higher biodegradation. Echevarría et al. (2019) removed only 80%

445   of ERY in an MBR system with an ultrafiltration membrane, since just 25 mg L^{-1} of

446   PAC were added.

447   Alvarino et al. (2017) also studied the roxithromycin and erythromycin removal on hybrid

448   PAC-MBR with microfiltration (MF) or ultrafiltration (UF) membranes and obtained

449   similar results to PAC-sMBR. Increments from 80% to above 95% and from 70% to

450   above 95%, for erythromycin and roxithromycin, respectively, were observed after PAC

451   addition until a final concentration of 750 mg L^{-1} in the MF-MBR (improvements of 16

452   and 26 %, respectively). In the case of UF-MBR, the removal percentages were from 90%

453   to above 99% in the case of erythromycin (9% of improvement), and from above 95% to

454   above 99%, in the case of roxithromycin (4% of improvement). Thus, the UF membrane

455   improved the effectiveness of the bioreactor for the emerging pollutants removal.

456   Likewise, the low K_d values for both antibiotics (Table 1) suggested that sorption onto

457   sludge was not remarkable, therefore, biodegradation and sorption onto activated carbon

458   can be considered as their main elimination ways.

459   Several authors have studied sulfamethoxazole removal in PAC-sMBR and PAC-MBR

460   systems. Li et al. (2011) achieved sulfamethoxazole (SMX) removal percentages from

461   64% for MBR system to 80-87% for PAC-MBR, working with PAC concentrations

462   below 100 and 1000 mg L^{-1}, respectively (percentages of improvement by the activated

463   carbon addition of 20 and 22%). Alvarino et al. (2016) studied the same configuration

464   observing null influence of the activated carbon. Echevarría et al. (2019) observed even

465   a negative effect of the activated carbon for 25 mg L^{-1} concentration (54 versus 60 %).

466   These studies where activated carbon did not exert a beneficial effect have in common

467   the lower concentration of SMX, 40 µg L^{-1} and 0.313 µg L^{-1} by Alvarino et al. (2016) and

468   Echevarría et al. (2019), versus 750 µg L^{-1} by Li et al. (2011). Therefore, adsorption of

469   SMX on activated carbon can be considered negligible (K_d value among 0.011 and

470   0.5 L gSS^{-1}), Table 1. In fact, Pomiès et al. (2013) suggested biodegradation is the main

471   pathway for the removal of this antibiotic.

472   In the case of trimethoprim, an improvement of 80% in its removal was observed in a

473   PAC-sMBR hybrid technology (1000 mg L^{-1} of PAC) versus 56% in a PAC-MBR

474   (750 mg L^{-1} of PAC) (Alvarino et al., 2017). In agreement, Serrano et al. (2011) and

475   Alvarino et al. (2016, 2017, 2020) observed null removal or below 20% for the biological

476   treatment, increasing above 87% after PAC addition. Therefore, the adsorption on

477   activated carbon is the main pathway, as inferred from the low K_d and K_{biol} values

478   (0.0254-0.33 L g MLSS^{-1} and 0.05- 0.22 L g MLSS^{-1} day^{-1}, respectively) Table 1.

479   **4.1.2.2. Removal of antidepressants**

480   Diazepam (DZP) was studied by Serrano et al. (2011) and Alvarino et al. (2016) in a

481   PAC-sMBR configuration and similar results were obtained. Increments from below 20%

482   to above 93% were obtained after PAC addition until a final concentration of 1000 mg

483   L^{-1}. The same authors studied the fluoxetine (FLX) removal under the same conditions

484   with similar results, elimination percentages from above 80% to above 98% with the

485   addition of PAC. The low improvement could indicate low hydrophobicity of FLX,

486   however, this does not agree with its log Kow value which, indicates a medium adsorption

487   on activated carbon trend, Table 1. Nevertheless, average K_d and K_{biol} values indicate that

488   adsorption onto activated sludge and biodegradation must be considered. Therefore, both

489   adsorption on activated carbon and sludge are the main FLX removal pathways, Table 1.

490   Comparing both pollutants, similar behaviour is observed when adding activated carbon,

491   due to the similar log Kow coefficients for both substances, 2.5-4. However, in absence

492   of the adsorbent, fluoxetine (FLX) was more easily eliminated than diazepam (DZP) due

493   to the higher K_d and K_{biol} values, Table 1.

494   **4.1.2.3. Removal of anti-inflammatory drugs**

495   Alvarino et al. (2017) also studied the elimination of diclofenac (DCF), ibuprofen (IBP)

496   and naproxen (NPX) by using a PAC-MBR system (microfiltration (MF) and

497   ultrafiltration (UF)) with a dosage of activated carbon until a final concentration of 500

498   mg L^{-1}. As a result, the removal percentage for NPX (from 75% to 96%, in absence and

499   presence of PAC) was independent of the filtration membrane. For DCF, a higher removal

efficiency was achieved in the biological system using a UF membrane than an MF

(removal percentages of 60% and 30%, respectively). In this case, the PAC incorporation

reached a removal percentage of 80%. Concerning IBP, the removal percentage of the

drug remained constant (75-100%) with no influence of the kind of membrane or the

absence/presence of the activated carbon. Echevarría et al. (2019) also studied the

elimination of DCF in a PAC-MBR system observing increases in purification from 72%

to 87 and 97 %, when introducing 25 and 50 mgL^{-1} activated carbon, respectively.

Therefore, a higher concentration of activated carbon enhances the performance of the

hybrid technology.

Finally, Serrano et al. (2011) and Alvarino et al. (2016, 2020) investigated the elimination

of DCF, IBP and NPX in a PAC-sMBR configuration by using a 1000 mg L^{-1} of PAC, a

hydraulic retention time (HRT) of 1 day and concentrations of MLVSS ranging from

3500 to 6000 mg MLVSS L^{-1}, from 4500 to 8000 mg MLVSS L^{-1} and 6000 mg MLVSS

L^{-1} for the first, second and third author, respectively. As a result, drug removal

percentages obtained were very similar in all cases. The percentages of DCF and NPX

removal varied from 20% to above 93% for DCF, and from 60% to above 78% for NPX,

after PAC addition. Regarding IBP, any improvement was obtained from the addition of

PAC and the elimination percentage was kept above 80%.

4.1.2.4.Removal of hormones

Alvarino et al. (2016; 2020) observed similar elimination percentages for estrone (E1),

17α- ethinylestradiol (EE2) and 17β-estradiol (E2) from 60-80% to above 98% by adding

PAC until a final concentration of 1000 mg L^{-1} in a sequential MBR system (PAC-sMBR

configuration).

523   Yang et al. (2010) and Alvarino et al. (2017) studied the elimination of EE2 and E2 in a

524   PAC-MBR configuration by addition of activated carbon until a final concentration of

525   500 - 2000 mg L^{-1} . In both cases, an increase in the elimination of hormones was observed

526   after activated carbon incorporation, from 60% to 82%.

527   Thus, the addition of activated carbon to the MBR technology further improves the

528   removal of hormones, even considering that the results were already noticeable (60 %).

529   This could be attributed to the high K_d and K_{biol} values presented by these hormones.

530   Furthermore, in accordance with the log Kow values, these hormones are easily adsorbed

531   on activated carbon, Table 1.

532   **4.1.2.5.Removal of other pharmaceuticals**

533   Several authors studied the elimination of atenolol (ATN) betablocker drug and

534   carbamazepine (CBZ) anticonvulsant though a PAC-MBR configuration.

535   Echevarría et al. (2019) studied the removal of ATN in a pilot scale PAC-MBR system

536   with an external ultrafiltration membrane. As a result, the elimination percentage of the

537   system improved from 95 %, in absence of the adsorbent, to 95 or 97 % in presence of

538   activated carbon at final concentration of 25 and 50 mgL^{-1}, respectively. From these

539   results, it is inferred that although activated carbon can enhance the performance of the

540   system, biodegradation is a significant pathway to the elimination of this compound.

541   Regarding the anticonvulsant group, CBZ elimination was studied in PAC-MBR by Li et

542   al. (2011) and Alvarino et al. (2017, 2020). Both authors observed a change in the

543   anticonvulsant removal percentage from 0 to above 88% when PAC was added in the

544   reactor, until a final concentration between 500 and 1000 mg L^{-1}. Even with lower carbon

545   concentration, from 25 to 50 mg L^{-1} in a PAC-MBR system, Echevarría et al. (2019)

546   observed CBM removal from 67 to 97 %, respectively. Comparison of PAC-sMBR and

547   PAC-MBR systems was carried out by Serrano et al. (2011) and Alvarino et al. (2016),

548   who observed similar results in the CBZ removal: from below 20%, in absence of PAC,

549   to above 96% for PAC final concentration of 1000 mg L^{-1}.

550   Considering these results, sorption onto PAC is the main removal route for

551   carbamazepine whereas biodegradation and sorption onto sludge are negligible

552   elimination pathways. This can be justified since the K_d and K_{biol} values for CBZ are

553   lower than the values reported by Pomiès et al. (2013), in which sorption onto activated

554   sludge and biodegradation can be neglected (below 0.11 L g MLSS^{-1} and 0.1 L g MLSS^{-}

555   ^{1} day^{-1}, respectively), Table 1.

4.1.3.   Application of BAC reactor

557   Elimination of four antibiotics (erythromycin (ERY), roxithromycin (ROX),

558   sulfamethoxazole (SMX), and trimethoprim (TMP)),) an anticonvulsant (carbamazepine

559   (CBZ)), an antidepressant (diazepam (DZP)) and three anti-inflammatory drugs

560   (diclofenac (DCF), ibuprofen (IBP) and naproxen (NPX)) were examined by Paredes et

561   al. (2016) in a fluidized-bed aerobic BAC reactor. The feed was up-flow operated and

562   contact times of 17 and 35 min were selected. As a result, removal percentages between

563   70 and 99 % were achieved at the lowest contact time. For the largest contact time,

564   elimination percentages obtained were in all cases above the 90 %. Additionally,

565   Fundneider et al. (2021) also studied the elimination of DCF for a contact time of 24.4

566   min, obtaining an intermediate elimination percentage (89 %). Therefore, removal

567   increases with contact time.

568   Similarly, Weemaes et al. (2011) reported removal percentages of 57, 33, 65, 71 and 84

569   % for TMP, CBZ, DCF, IBP and NPX with a contact time of just 13 minutes.

570   Furthermore, the applied system was a GAC fluidized bed reactor (without

571   microorganisms) and downflow-fluid operated. Thus, the synergic effect of

572   biodegradation and physical adsorption, as well as the best performance of the upflow

573   mode, could also justify the best results obtained by Paredes et al. (2016) versus Weemaes

574   et al. (2011).

575   Gerrity et al. (2011) managed to eliminate 99 % of SMX in a BAC system with a contact

576   time of only 30 min. The applied ozonation prior to the BAC operation could improve its

577   performance. Thus, SMX and some substances, which could mitigate the bioactivity of

578   the biofilm, could been partially removed enhancing the effectivity of this configuration.

579   Ho et al. (2011) studied the elimination of two hormones, E1 and EE2, in a BAC fluidized

580   reactor and, after a contact time of 15 min. An elimination greater than 99% was achieved

581   during the first 100 days of operation, decreasing from that moment. Therefore, a long

582   operating time can lead to an inadequate development of the biofilm that could prevent

583   the transfer of hormones from the liquid phase to the surface of the activated carbon

584   (Paredes et al., 2016).

585   **4.2. Removal of personal care products (PCPs)**

586   **4.2.1.   Application of PACT/GAC-CAS reactors**

587   Serrano et al. (2010) studied celestolide (CEL), galaxolide (GAL) and tonalide (TON)

588   musk fragrances through a GAC-CAS configuration with a GAC final concentration of

589   1000 mg L^{-1} in the reactor. No improvements in the elimination of these substances were

590   observed after de GAC addition, since the removal percentage remained between 71 and

591   92% in all cases.

592   Boehler et al. (2012) studied the UV filter diethylamino hydroxybenzoyl hexyl benzoate

593   (DHHB) in a PACT configuration with PAC concentrations of 15 and 30 mg L^{-1} in the

594   CAS bioreactor. The DHHB removal percentage increased from 20-30% in absence of

595   PAC up to 65-75% or the 80-90% with the addition of PAC, so adsorption onto activated

596   carbon can be considered as its main elimination route. This can be confirmed with its

597   log Kow value (Table 1), which indicates the high hydrophobicity of the substance.

4.2.2. Application of an PAC-MBR reactor

599   Alvarino et al. (2016) studied celestolide (CEL), galaxolide (GAL) and tonalide (TON)

600   through a PAC-sMBR system. The presence of PAC at 1000 mg L^{-1} resulted in an

601   increase of the removal percentages from above 80% to above 98 % in the cases of CEL

602   and GAL, and from 40-60% to above 98% for TON. The low elimination percentage in

603   absence of the carbonaceous adsorbent for this last micropollutant can be explained since

604   TON presents the lowest biodegradation rate constant (0.023 L g $MLSS^{-1}$ d^{-1}) and,

605   therefore, the biodegradation removal route can be considered as less important than for

606   the other substances.

4.3.   Removal of other emerging pollutants

608   Boehler et al. (2012) studied the elimination of two anticorrosive agents (benzotriazole

609   (BT) and 5-methyl-1H-benzotriazole (5-Ttri)) in a PACT configuration by adding 15 and

610   30 mg L^{-1} concentrations of PAC in a CAS reactor. Independently of PAC concentration,

611   the removal percentage of BT and 5-Ttri changed from 30-40% and 50-60% in absence

612   of activated carbon up to above 80% and 90-95% in presence of PAC, respectively.

613   Although, for these anticorrosive agents, the log K_{ow} values reported in literature indicate

614   that adsorption on activated carbon could be negligible, these results must be considered.

615   Regarding the biodegradation elimination pathway, Liu et al. (2011) aimed that BT

616   showed a slow biological degradation in aerobic conditions (K_{biol} of 0.22 L g $MLSS^{-1}$

617   day^{-1} (Mazioti et al., 2017)) whereas for 5-Ttri, the biodegradation route is the most

618 remarkable. Furthermore, the low K_d value for BT (Table 1) implied that adsorption onto

619 activated sludge can be a negligible route for the elimination of this compound.

620 Baumgarten et al. (2007) studied an impurity of fluoroquinolones antibiotics

621 (fluoroquinolonic acid) in a PAC-MBR system. Removal percentages of this compound

622 ranged from 27% to 77% or 94% when PAC was added until final concentrations below

623 50 mg L^{-1} and among 50-200 mg L^{-1}, respectively. From these results, sorption onto

624 activated carbon can be considered as a significant elimination pathway (log Kow of

625 2.31).

626 Several adsorption/biological hybrid configurations for the removal of pharmaceutical,

627 personal care products and other emerging pollutants in wastewater have been examined

628 in this review. PAC-MBR and PACT systems are the most applicable techniques in this

629 field followed by BAC and GAC-CAS configurations. Considerable better performances

630 were obtained in comparison with single techniques by observing the micropollutant

631 elimination percentages in absence and presence of activated carbon. Specifically, PAC-

632 MBR results in reaching the highest removal percentages for the majority of emerging

633 pollutants (from 81 to 98%). Furthermore, it was observed that the efficiency of an hybrid

634 adsorption/biological technology is determined by the strength of the interaction of the

635 pollutant compound with the activated carbon. Best results were obtained for

636 micropollutants with dipole moments (μ) lower than 6 debyes. In case of molecules with

637 μ higher than 6 debyes, the value of log Kow becomes relevant, since a log Kow value

638 higher than 3 is required to consider a successful hybrid process.

639 Concerning the economical evaluation of the hybrid techniques reported in this study,

640 PAC-MBR presents the highest capital expenditure, followed by PACT and BAC

641 technologies. However, the low value of BAC can be attributed to a lower equipment

642   consideration during the development of the study, indicating that PACT can be the most

643   favourable technology in economic terms.

644   The activated carbon requirements for an hypothetical plant with a capacity of 10000 m^3

645   d^{-1}, in increasing order, were 7 kg m^{-3} for PACT<339 kg m^{-3} for BAC<377 kg m^{-3} for

646   PAC-MBR systems. Since BAC is the only configuration which uses GAC, which is

647   considerably more expensive than the PAC, this technology could imply considerably

648   higher economical requirements than PACT or PAC-MBR systems. The high activated

649   carbon requirements of PAC-MBR technique can be justified since no data at real scale

650   were used for carrying out the scale-up.

651   Finally, although PAC-MBR technology can be considered the most promising technique

652   in terms of removal percentages achieved, PACT is a more economical configuration

653   since it presents lower CAPEX and activated carbon requirements.

654

655

656   **5. DISCUSSION   ON   THE   INFLUENCE   OF   PHYSICOCHEMICAL**

657   **PROPERTIES OF ADSORBATES AND COMPARATIVE PERFORMANCE**

658   **OF HYBRID SYSTEMS**

659   From section 4, and results summarized in Table 2, it is clearly observed that there is not

660   an homogeneous behaviour for the different emerging pollutants removal by the hybrid

661   technologies. Wastewater quality, organic matter concentrations and operation conditions

662   data (Table 3) were quite similar for the reviewed technologies. However, improved

663   efficiency by the addition of the activated carbon in the media can vary significantly

664   (green cells in Table 2) or practically not affect (yellow cells). Thus, it is logical to

665 attribute these differences to either, the morphology and surface chemistry of the

666 adsorbent, or the adsorbate characteristics. Considering that the activated carbon used in

667 all operations is a similar material, mainly characterized by its high surface area and the

668 presence of micropores, the size and presence of functional groups in the emerging

669 pollutants molecules is supposed to be the key. At this point, in a previous work it was

670 observed that the strength of the interaction of emerging pollutants on an activated carbon,

671 that is, the enthalpy of adsorption, matched with the decreasing order of molecular polar

672 surface area (Patiño et al., 2015). So, the presence of functional groups in the adsorbate

673 hindered the adsorption, avoiding the entrance of the adsorbate into the micropores of the

674 activated carbon. With these antecedents, it seems logical to think that a parameter that

675 measures the polarity of the molecules, dipole moment, μ, could be a good

676 physicochemical predictive indicator of the hybrid technologies success. Likewise,

677 enthalpy of adsorption of emerging pollutants was observed to increase with the octanol–

678 water partition coefficient. With these premises, an exhaustive analysis of those pollutants

679 whose biological degradation was less effective (efficiency $< 80\%$) was carried out. This

680 limit was chosen since degradation systems are considered successful in the organic

681 micropollutants removal over this value (Lema and Suarez, 2017). Figure 2 shows the

682 influence of both, the dipole moment and the octanol–water partition coefficient, on the

683 emerging pollutant removal efficiency of the hybrid adsorption-biological removal

684 process.

685 In this plot, where PAC-MBR configuration data is presented, green dots represent the

686 most favourable situation for hybrid technology: micropollutants removal above 90% and

687 improvement above 20% after activated carbon incorporation. As it can be observed,

688 micropollutants with low dipole moments, lower than 6 debyes, can be considered in all

689   cases as successful; whereas for $\mu > 6$ debyes, the value of log Kow becomes relevant,

690   since a log Kow > 3 is required to consider a successful hybrid process.

691   So, it is shown that the efficiency of the hybrid process is determined by the strength of

692   the interaction of the pollutant compound with the activated carbon, and the dipolar

693   moment and the octanol-water partition coefficient can predict the possible success of the

694   incorporation of the adsorbent in the biological process.

695   If we focus now on the type of technology, Table 2 exhibits the removal performance of

696   34 emerging pollutants by the different adsorption/biological hybrid configurations under

697   study, being PAC-MBR configuration the most applied (21 of the 34 micropollutants of

698   study), followed by PACT, BAC and GAC-CAS. The development degree is also

699   different. PACT and BAC have been implanted at industrial scale, since PACT is the

700   most mature technique (Reife and Freeman, 1996; Meidl, 1997); whereas BAC has been

701   implemented but for drinking water treatment plant instead of wastewater (Cuthbertson

702   et al., 2020). On the other hand, both PAC-MBR (Alvarino et al., 2017; Hu et al., 2017;

703   Echevarría et al., 2019) and GAC-CAS (Sirianuntapiboon, 2002; Sirianuntapiboon and

704   Sansak, 2008) have been widely studied at lab and pilot scale.

705   Considering the evaluation of the efficiency of the different hybrid technologies (green

706   cells in Table 2), PACT and PAC-MBR are the most repeated options as preferred

707   technology. At this point, it is important to remark that PAC-MBR is the most recurrent

708   preferred technique. Thus, PAC-MBR despite being a more recent technology, it would

709   stand out as the most promising. An incentive for the development and implementation

710   of PAC-MBR technology is the better removal of organic compounds by including a

711   membrane in the biological system in comparison with CAS biological reactors (Kimura

712 et al., 2007; Kraume and Drews, 2010) and also it does not require the secondary settler

713 since the membrane performs the solid-liquid separation (Judd, 2010).

714

6. ECONOMICAL EVALUATION OF DIFFERENT ADSORPTION/BIOLOGICAL DEGRADATION HYBRID TECHNOLOGIES

717 An evaluation of the capital cost of PACT, PAC-MBR and BAC configurations has been

718 carried out through the analysis of the capital expenditure (CAPEX). In that way, Table

719 4 summarized the capital expenditure of CAS, MBR and GAC systems. CAPEX of CAS

720 systems was considerably heterogeneous since in some cases it is considered equipment

721 and project construction (machinery, civil work and electric measurement) costs of a

722 complete CAS wastewater treatment plant and, in other cases, only the biological

723 treatment of the process (Wozniak, 2012; Young et al., 2012; Jafarinejad, 2017b) (Table

724 4). For MBR configuration, data reported just consider the equipment costs of the

725 biological reactor and the membrane system (Wozniak, 2012; Young et al., 2012; Lo et

726 al., 2015; Lema and Suarez, 2017). However, quite different data have been published

727 depending on the membrane used.

728 Calculation of each hybrid technology was based on the addition of CAS or MBR systems

729 CAPEX to the PAC cost, assuming the equipment cost of an extra adsorbent tank and a

730 settler to separate part of the PAC from sludge (Mulder et al., 2015). The volume variation

731 due to the introduction of activated carbon was negligible since the increase of reactor

732 volume was below 1% in all cases. This value was calculated for PACT and PAC-MBR

733 based on the activated carbon concentration and reactor volumes reported for wastewater

734 treatment plants (Serrano et al., 2010; Li et al., 2011; Serrano et al., 2011; Alvarino et al.,

735 2016; Alvarino et al., 2017). In the case of PACT, the biological reactor and secondary

736   settler are considered as main equipment, which represents 39% of the CAPEX for those

737   cases where construction costs were included (Young et al. 2012; Jafarinejad, 2017b).

738   CAPEX's data from the BAC configuration (Table 4) were applied by considering the

739   capital costs for the construction of a GAC system where GAC filter structure, filter

740   media, backwash pumping, intermediate lift pumping, yard piping, site work, and

741   electrical and control systems were considered (Plumlee et al., 2014; Mulder et al., 2015).

742   Finally, the CAPEX values have been actualised to 2019 year by the annual CEPCI

743   indexes from Chemical Engineering Journal (Scott, 2015a, 2015b, 2020).

744   With these antecedents, Figure 3 shows calculated data for the different hybrid

745   configurations with confidence intervals. Literature information used to elaborate this

746   Figure has been included in Table S.3.

747   Likewise, data reported fit to the following potential equations for PACT, PAC-MBR and

748   BAC technologies, respectively:

$$CAPEX_{PACT} = 0.2403 \cdot Capacity^{0.3801} \qquad R^2 = 0.9716 \qquad (1)$$

$$CAPEX_{PAC-MBR} = 5 \cdot 10^{-4} \cdot Capacity^{1.1613} \qquad R^2 = 0.9715 \qquad (2)$$

$$CAPEX_{BAC} = 6 \cdot 10^{-5} \cdot Capacity^{0.919} \qquad R^2 = 0.9976 \qquad (3)$$

749   From these results, it was observed that BAC technology has the lowest CAPEX due to

750   the less equipment considered in comparison with other technologies. For PACT and

751   PAC-MBR, similar CAPEX results were obtained at low capacities (below 2700 $m^3 d^{-1}$).

752   However, the PAC-MBR CAPEX grows up largely with the capacity due to the

753   membrane cost. In fact, separation units represent 16-25% of the total CAPEX in CAS

754   due to the secondary settler, whereas the 30-39% in an MBR system (Young et al., 2012).

755   These results were in accordance with Hao et al. (2018) and Yang et al. (2020), who

756 observed CAPEX values considerably lower for PAC than for MBR technologies when

757 5000-10000 $m^3 d^{-1}$ of wastewater and 920 $m^3 d^{-1}$ of textile wastewater, respectively, were

758 treated. Furthermore, PACT seems to be the most favourable technology to be installed

759 in a pre-existent plant, since over 90% of the WWTPs use activated sludge reactors as

760 secondary treatments (Liu, 2003).

761 Finally, for an hypothetical plant with a capacity of 10000 $m^3 d^{-1}$, the concentration of

762 activated carbon, according to the literature requirements (Table 5), decreases in the

763 order: PAC-MBR (377 kg m^{-3}) > BAC (339 kg m^{-3}) > PACT (7 kg m^{-3}) (Reife and

764 Freeman, 1996; Meidl, 1997; Wilson et al., 1998; Song et al., 2006; Reungoat et al., 2010;

765 Serrano et al., 2010; Ho et al., 2011; Li et al., 2011; Serrano et al., 2011; Weemaes et al.,

766 2011; Boehler et al., 2012; Alvarino et al., 2016; Mailler et al., 2016; Paredes et al., 2016;

767 Alvarino et al., 2017; Echevarría et al., 2019). At this point, it is convenient to remark

768 that the BAC technology uses granular activated carbon, which is considerably more

769 expensive than powered one (17.5 USD kg^{-1} versus 0.995 USD kg^{-1} found in Alibaba

770 commerce company) (Alibaba, 2020a; Alibaba, 2020b). Furthermore, the high activated

771 carbon requirements in the PAC-MBR technology can be attributed to the scale change

772 made from pilot and laboratory scale data, while in PACT and BAC full scale data were

773 used (Table 5 capacity ranges are shown).

774

775 **7. FUTURE CHALLENGES**

776 Adsorption-biological hybrid systems have resulted to perform better than single

777 technologies to eliminate emerging pollutants. Elimination percentages above 80 % were

778 obtained for most of the reviewed emerging pollutants. However, full removal of the most

779 recalcitrant emerging pollutants has not been achieved. Thus, some future perspectives

780 regarding this field must be considered:

781 - Taking into account that the interaction of the emerging pollutant with the adsorbent

782 plays a key role, the study or modification of the adsorbent surface to increase the strength

783 of the interaction could be the starting point. At this point, Kim et al., 2019 proposed

784 using activated biochars instead of commercial activated carbons with promising results.

785 Thus, the performance of adsorption-biological hybrid technologies based on activated

786 biochars, instead of a commercial activated carbon, can provide key improvements for

787 the EPs removal.

788 -Application of micro-granular activated carbon (µGAC) to CAS and MBR technologies

789 apart from conventional adsorption tertiary treatments. µGAC could be a suitable option

790 since this type of GAC has achieved MPs elimination performances similar to PAC with

791 the same activated carbon dose when activated carbon was used as a tertiary treatment

792 after a biofiltration secondary treatment (Mailler et al., 2016).

793 -Exploring some new hybrid technology combining more than two technologies. For

794 example, the application of activated carbon to reverse osmosis and biological treatment

795 (osmotic membrane bioreactors) has been recently developed as a promising technology

796 for the removal of emerging pollutants. (Dhangar and Kumar, 2020).

797 -Study of new systems which applied nanoscale science or genetic engineering which

798 could somehow improve the degradation of still recalcitrant micropollutants.

799 Future studies on the performance of these technologies applied to other treatment plants,

800 like drinking water or reclamation plants, and other groups of micropollutants, like

801   fertilizers, biocides and more recent EPs such as microplastics or nanoparticles, could be

802   interesting.

803   Finally, more detailed experiments applying hybrid technologies at an industrial scale

804   should be carried out. Thus, wide studies on the reaction and adsorption kinetic of the

805   EPs and more specified information about reactor designs and operational conditions

806   applied to real scale adsorption-biological systems must be considered.

807

808   **8. CONCLUSIONS**

809   Several adsorption/biological hybrid configurations for the removal of pharmaceutical,

810   personal care products and other emerging pollutants in wastewater have been examined

811   in this review. PAC-MBR and PACT systems are the most applicable techniques in this

812   field followed by BAC and GAC-CAS configurations. Considerable better performances

813   were obtained in comparison with single techniques by observing the micropollutant

814   elimination percentages in the absence and presence of activated carbon. Specifically,

815   PAC-MBR results in reaching the highest removal percentages for the majority of

816   emerging pollutants (from 81 to 98%). Furthermore, it was observed that the efficiency

817   of a hybrid adsorption/biological technology is determined by the strength of the

818   interaction of the pollutant compound with the activated carbon. Best results were

819   obtained for micropollutants with dipole moments (μ) lower than 6 debyes. In the case of

820   molecules with μ higher than 6 debyes, the value of log Kow becomes relevant, since a

821   log Kow value higher than 3 is required to consider a successful hybrid process.

822   Concerning the economical evaluation of the hybrid techniques reported in this study,

823   PAC-MBR presents the highest capital expenditure, followed by PACT and BAC

824   technologies. However, the low value of BAC can be attributed to a lower equipment

825 consideration during the development of the study, indicating that PACT can be the most

826 favourable technology in economic terms.

827 The activated carbon requirements for a hypothetical plant with a capacity of 10000 m^3

828 d^{-1}, in increasing order, were 7 kg m^{-3} for PACT<339 kg m^{-3} for BAC<377 kg m^{-3} for

829 PAC-MBR systems. Since BAC is the only configuration which uses GAC, which is

830 considerably more expensive than the PAC, this technology could imply considerably

831 higher economical requirements than PACT or PAC-MBR systems. The high activated

832 carbon requirements of PAC-MBR technique can be justified since no data at real scale

833 were used for carrying out the scale-up.

834 Finally, although PAC-MBR technology can be considered the most promising technique

835 in terms of removal percentages achieved, PACT is a more economical configuration

836 since it presents lower CAPEX and activated carbon requirements.

837

843

844 **Credit author statement**

845 Laura García: Original Draft, Data curation, Reviewing, Editing, Formal

846 interpretation.

847   Juan Carlos Leyva: Reviewing, Formal interpretation.

848   Eva Díaz: Editing, Visualization, Conceptualization, Project administration.

849   Salvador Ordóñez: Visualization, Conceptualization, Supervision, Funding

850   acquisition.

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Nomenclature

1455

1456 **Nomenclature**

1457 μ: Dipole moment

1458 μGAC: micro-granular activated carbon

1459 5-Ttri: 5-methyl-1H-benzotriazole

1460 AOPs: Advanced oxidation processes

1461 BAC: Biofilm or biological activated carbon

1462 BAC-FBR: Biological activated carbon in a fluidized-bed reactor.

1463 BOD: Biological oxygen demand

1464 BT: Benzotriazole

1465 CAM: Clarithromycin

1466 CAPEX: Capital expenditure

1467 CAS: Conventional activated sludge

1468 CBZ: Carbamazepine

1469 CEL: Celestolide

1470 COD: Chemical oxygen demand

1471 COE: Codeine

1472 DCF: Diclofenac

1473 DHHB: Diethylamino hydroxybenzoyl hexyl benzoate

1474 DOC: Dissolved organic compounds

1475 DZP: Diazepam

1476 DZP: Diazepam

1477 EBCT: Empty bed contact time

1478 E1: Estrone

1479 E2: 17β-estradiol

1480   EE2: 17α-ethinylestradiol

1481   ENR: Enrofloxacin

1482   EPs: Emerging pollutants

1483   EPS: Extracellular polymeric substances

1484   ERY: Erythromycin

1485   FLX: Fluoxetine

1486   GAC: Granular activated carbon

1487   GAC-CAS: Granular activated carbon-conventional activated sludge system

1488   GAC-FBR: Granular activated carbon in a fluidized-bed reactor

1489   GAL: Galaxolide

1490   HRT: Hydraulic retention time

1491   IBP: Ibuprofen

1492   IOH: Iohexol

1493   IOP: Iopromide

1494 K_{biol}: Biodegradation rate constant

1495 K_d: Solid-water distribution coefficient

1496   log Kow: Logarithm of the octanol-water partition coefficient

1497   MBR: Membrane bioreactor

1498   MF: Microfiltration

1499   MFA: Mefenamic acid

1500   MLSS: Mixed liquor suspended solids

1501   MLVSS: Mixed liquor volatile suspended solids

1502   NPX: Naproxen

1503   O&M: Operation and maintenance

1504   OXA: Oxazepam

1505   PAC: Powdered activated carbon

1506   PAC-MBR: Powdered activated carbon- membrane bioreactor system

1507   PAC-sMBR: Powdered activated carbon-sequential membrane bioreactor system

1508   PACT: Powdered activated carbon treatment

1509   PCPs: Personal care products

1510   PFCs: Perfluorinated compounds

1511   PR: Primidone

1512   ROX: Roxithromycin

1513   SBR: Sequential batch reactor

1514   SMX: Sulfamethoxazole

1515   SMX: Sulfamethoxazole

1516   SRT: Sludge retention time

1517   TMP: Trimethoprim

1518   TON: Tonalide

1519   TPs: Transformation products

1520   UF: Ultrafiltration

1521   VEN: Venlafaxine

1522   WWTPs: Wastewater treatment plants