1 **Integral evaluation of granular activated carbon at four stages of a full-scale**

2 **WWTP deodorization system**

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10 **Abstract**

11 Odor emissions from wastewater treatment plants (WWTPs) have always been a public

12 concern. In this work, the physico-chemical, olfactometric and textural characterization

13 of granular active carbon (GAC) used by an urban WWTP as a deodorization system, as

14 well as the chromatographic quantification of the retained odoriferous compounds, have

15 been carried out. These techniques have allowed an integral evaluation of the

16 contaminated GAC and the characterization of the retained gaseous emission from four

17 different stages of the wastewater treatment (pretreatment header: GAC-1; sand and fat

18 removal: GAC-2; sludge thickening: GAC-3; sludge dehydration: GAC-4). A larger

19 amount and variety of retained odoriferous compounds were found in GAC samples

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Abbreviations: D_{pore}, average pore width (nm); GAC, granular activated carbon; GC, gas chromatography; MS, mass spectrometry; OAV, odor activity value; OC, odor concentration (ou_E/m^3); ODT, odor detection threshold ($\mu g/m^3$); ou_E, European odor units; PC_i, chemical contribution (%); PO_i, odor contribution (%); S_{BET}, specific surface area (m^2/g); S_{micro}, micropore area (m^2/g); SOC, removed specific odor concentration ($ou_E/m^3 \cdot g$ GAC); TC, total concentration of desorbed gaseous compounds ($\mu g/g$ GAC); TD, thermal desorption; TN_s, soluble total nitrogen (mg/g GAC); TOC, soluble total organic carbon (mg/g GAC); V_{micro}, free micropore volume (cm^3/g); VOCs, volatile organic compounds; V_t, total pore volume (cm^3/g); WWTPs, wastewater treatment plants; XRF, X-ray fluorescence.

from the wastewater line deodorization (GAC-1 and GAC-2) after the same operation

time (one year), GAC-1 being the adsorbent bed that retained the greatest mass of

volatile compounds (approximately 150 µg/g GAC). Furthermore, some variables such

as the removed specific odor concentration and free micropore volume were inversely

correlated ($R^2 = 0.9945$). The analysis of odor contribution showed that sulfur-

containing compounds were the major odor contributors (61–97%). However, hydrogen

sulfide cannot be considered a key odorant in this particular WWTP, since the

elimination of this compound does not reduce the significant contribution of other

(organic) sulfur compounds to the global odor (especially dimethyl disulfide).

Consequently, multi-technical analysis might be a suitable alternative to better

understand odor removal by GAC adsorption.

Keywords: emitted gaseous compounds; granular activated carbon; multi-technical

analysis; odor contribution; WWTP.

1. Introduction

Odor emissions have traditionally had a secondary role in global environmental

policies. Nevertheless, it is well known that long-term exposure to odorants can cause

diverse negative effects on human health, such as headaches, nausea and vomiting,

insomnia, respiratory tract alterations, irrational behavior and even cancer (Byliński et

al., 2019b; Domingo and Nadal, 2009). For this reason, the odor impact caused by

industrial activities and waste management has become increasingly important in

international environmental regulations. The inclusion of odor impact in the second

draft of the Biowaste Directive of 2001 is one such example (European Commission,

2001). The odoriferous impact of wastewater treatment plants (WWTPs) is the source of

many complaints and protests in nearby residential areas (Easter et al., 2008; Hayes et

al., 2017; Morales et al., 2008). This is due to the large number of volatile odorants present in the gaseous emissions from these facilities, some of which have very low odor threshold values in terms of ppb_v or ppt_v (Nagata, 2003). Hydrogen sulfide is commonly considered to be the main compound responsible for the odor impact of WWTPs (Talaiekhozani et al., 2016). Gaseous emissions from WWTPs also contain other sulfur compounds such as mercaptans, organic compounds (e.g., butyric acid, butanone, toluene, benzene and skatole), ammonia and nitrogen derivates such as amines (Fisher et al., 2018; Lebrero et al., 2011; Talaiekhozani et al., 2016).

In WWTPs, it is not only important to identify the compounds which cause malodor problems, but also the areas of these facilities that contribute most to odor impact. According to Lebrero et al. (2011), primary treatments (e.g. various kinds of grilles or initial settling tanks) and sludge handling activities constitute the main odor sources in WWTPs. By means of odor emission factors, Capelli et al. (2009) predicted odor emissions from WWTPs, highlighting primary sedimentation, pretreatments and sludge thickening as the main odor sources. Gebicki et al. (2016) also reported the average percentage distribution of odour emission sources from a sewage treatment plant: preliminary operations (53.5%), sludge dewatering, drying and thickening (36.6%), rinsing (6.2%), tank aeration (1.8%), fermentation tanks (1.4%) and clarifiers and sand traps (0.5%). Therefore, odor control strategies should focus especially on the first two sources, which may jointly account for up to 90% of emissions which can affect the occurrence of malodor in surrounding areas.

In general, odor control in sewage treatment plants includes (i) prevention of odorant formation and emission; and (ii) elimination of malodor compounds by means of end-of-the-pipe odor abatement systems (Talaiekhozani et al., 2016; Tchobanoglous et al., 2003). Prevention should be the priority strategy. However, this is a difficult task

69   because compounds, such as sulfides, are already present in the wastewater reaching

70   WWTPs (and subsequently transferred to the gaseous phase) or the result of existing

71   design parameters. In the latter case, the solution would be a correct plant design, which

72   requires a high capital investment. On the other hand, there are also simpler and less

73   costly prevention operations such as the regular cleaning of screening units or grit

74   chambers (Lebrero et al., 2011). When prevention is insufficient to mitigate nuisance

75   emissions, odor treatment technologies must be applied. The nature and concentration

76   of odorants, the required efficiency and the air flow rate to be deodorized are among the

77   variables that influence the selection of a specific treatment system. Hence, different

78   physico-chemical and biological methods might be of interest (Burgess et al., 2001).

79   Adsorption by granular activated carbon (GAC) is a reliable and well-established

80   physico-chemical technique for treating odors in WWTPs due to its capability to easily

81   adsorb a wide range of odorants, such as volatile organic compounds (VOCs),

82   mercaptans, ammonia and hydrogen sulfide (Le-Minh et al., 2018; Lebrero et al., 2011).

83   The replacement of GAC beds is based on empirical experience because GAC

84   manufacturers do not often guarantee the adsorbent life of GAC beds in WWTP

85   applications (Estrada et al., 2011). In this context, both odor removal efficiency and

86   filter replacement are often based on H_2S removal. According to Jiang et al. (2017), H_2S

87   is a key odorant in WWTPs, and the concentration of this compound is easily

88   measurable in situ using online sensors (Lebrero et al., 2011; Martin et al., 2010).

89   However, the deodorization of gaseous effluents from WWTPs requires the removal of

90   a complex mixture of compounds with a wide range of molecular weights, volatilities

91   and chemical functionalities. For instance, other malodorous volatile sulfur compounds

92   beyond H_2S (dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, etc.) are widely

93   reported in the literature (Watson and Jüttner, 2017). Therefore, analytical and sensory

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94   measurements should be combined to ensure the optimal design of deodorization

95   operations (Martin et al., 2010).

96   In line with the above, this work proposes an integral evaluation of the GAC from the

97   deodorization system of an urban WWTP and the characterization of the retained

98   gaseous emission from four different stages of the integral wastewater treatment. For

99   this purpose, physico-chemical, olfactometric and textural characterizations of the GAC

100   used by the facility as an odor treatment system, as well as the chromatographic

101   quantification of the retained odoriferous compounds, were carried out. To the best of

102   our knowledge, a multi-technical analysis to better understand the odor removal process

103   by GAC adsorption has not been previously reported in the literature. This information

104   might aid in optimizing GAC operations in WWTPs that employ this deodorization

105   system, with the consequent benefits for occupational health within the WWTP and the

106   reduction of odor impact in the nearby population.

107   **2. Material and methods**

108   *2.1. WWTP: Description of the activity*

109   The urban WWTP of this study is located in the province of Seville, Spain, and has the

110   capacity to treat wastewater from a population equivalent of 950,000. The facility has a

111   current treatment capacity of 255,000 m^3/d and operates with a biological secondary

112   treatment (active sludge) and the treatment of sludge stabilization by anaerobic

113   digestion and dehydration. It carries out anaerobic co-digestion of sewage sludge with

114   other agrifood waste. Figure 1 shows the schematic flow diagram of the facility.

115   The WWTP under study uses GAC adsorption as a deodorization system. In addition, in

116   order to avoid the presence of H_2S in the biogas produced in anaerobic digesters, ferric

117   chloride ($FeCl_3$) is added to the wastewater line (before sludge thickening), which reacts

118 with H_2S to form an iron-sulfide precipitate (Fe_2S_3), which settles quickly in quiescent

119 conditions (Water Environment Federation, 2017).

120 *2.2. Granular activated carbon: description and operation*

121 For purposes of the present study, four contaminated samples of the same GAC from

122 different WWTP locations were provided by the facility. The four GAC samples had the

123 same operation time (one year). In the central part of each deodorization bed, 9

124 replicates per sample were taken, in accordance with an experimental design of a regular

125 cube centered on the origin and avoiding the input and output surface of the GAC bed.

126 The 9 replicates of approximately 200 g each were homogenized and fractionated into 3

127 new replicates, with which the present study was carried out. The samples were kept

128 cold during transportation and stored at 6 ± 2 ºC to prevent desorption of the retained

129 gaseous compounds. The origin of the samples and a description of the deodorization

130 towers are shown in Table 1. The pristine GAC (GAC-0) was made from coconut shell.

131 The manufacturer's technical specifications of GAC-0 were iodine number (minimum):

132 1000 mg/g; average particle diameter: 3.7 mm and ash content: 4%.

133 In the WWTP locations mentioned in Table 1, polluted air is sucked in by fans until it

134 reaches the active carbon filters, where malodor compounds are adsorbed.

135 Subsequently, clean air is expelled into the atmosphere through chimneys. The

136 hydrogen sulfide concentration at the system output is the most frequently used

137 parameter in this WWTP to proceed with the replacement of the adsorbent material. To

138 carry out this measurement, a portable analyzer (4000 series) manufactured by Interscan

139 Corporation is used. Contaminated GAC is considered a hazardous waste (code: 06 13

140 02) by the European Commission (2018) and is deposited in landfill and replaced by

141 fresh activated carbon (GAC-0).

142 *2.3. Characterization of the GAC samples*

143 For the different physico-chemical, textural, olfactometric and chromatographic

144 experiments, three replicates per GAC sample were used.

145 *2.3.1. Physico-chemical characterization*

146 *2.3.1.1. Acidic and basic surface groups*

147 The Boehm method (Boehm, 1994) was used to determine the concentration of both

148 basic and acidic remaining surface functional groups present in the GAC samples. To

149 quantify the concentration of basic groups (in mmol per gram of adsorbent), the samples

150 (0.25 g each) were added to a 50 mL hydrochloric acid solution (0.1M concentration)

151 and stirred for 48 hours at 170 rpm and 25 ºC. The suspension was then filtered and

152 three aliquots (3 mL each) of the filtrates were back titrated using a 0.1M NaOH

153 solution (in order to neutralize the excess acid) and phenolphthalein as an indicator. To

154 quantify the concentration of the acidic groups, the GAC samples were added to a 50

155 mL sodium hydroxide solution (0.1M) and stirred under the same conditions described

156 above. The suspension was then filtered and three aliquots of the filtrates were back

157 titrated using a 0.1M HCl solution in order to neutralize the excess base.

158 *2.3.1.2. Elemental composition*

159 The elemental composition (Na, K and S) of the GAC samples was determined by X-

160 ray fluorescence (XRF). Spectra were obtained using a Rigaku Wavelength Dispersive

161 X-ray Fluorescence (WDXRF) spectrometer (ZSX Primus IV model). The system is

162 equipped with a 4 kW rhodium target X-ray tube (operating at a maximum voltage of 60

163 kV and a current of 150 mA), ten analyzer crystals, a flow proportional counter for

164 detecting light elements and a scintillation counter for detecting heavy elements.

165 *2.3.1.3. TOC, TN_s, pH and conductivity*

166 The methodology proposed by the US Department of Agriculture and the US

167 Composting Council (2002) was used to quantify, in triplicate and in the aqueous

168 extract (1:25 ratio), the following variables: soluble total organic carbon (TOC, mg/g

169 GAC), soluble total nitrogen (TN_s, mg/g GAC), pH and conductivity (mS/cm).

170 *2.3.2. Determination of the textural properties*

171 The nitrogen adsorption/desorption data were obtained at the liquid nitrogen

172 temperature (77 K) using a Micromeritics ASAP 2020 M apparatus. The specific

173 surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) equation

174 in a relative pressure range of 0.04–0.20. Total pore volume (V_t) was calculated at

175 relative pressure $p/p_0 = 0.98$. The t-plot method was used to estimate the micropore area

176 (S_{micro}). Micropore volume (V_{micro}) was calculated according to the Dubinin-

177 Radushkevich equation (Nguyen and Do, 2001). The average pore width (D_{pore}) was

178 determined by the 4V/A following the BET method.

179 *2.3.3. Olfactometric measurements*

180 To desorb the odoriferous compounds adsorbed on the GAC samples and subsequently

181 quantify their removed specific odor concentration (SOC, $ou_E/m^3 \cdot$ g GAC), 0.5 g of each

182 sample was introduced into 20 mL glass bottles. After that, they were sealed and

183 maintained under isothermal conditions for 24 h. Then, the above mentioned bottles

184 were introduced into 4-L Nalophan® sampling bags. Once inside the bags, glass bottles

185 were opened for 15 minutes (equilibrium time) and then closed again. The next step was

186 to fill the bags with odorless compressed air at a filling time of 30 s. Finally, the

187 sampling bags were also kept in isothermal conditions until the determination of their

188 odor concentration. In order to evaluate the variation in SOC with the increase in

189 temperature, five desorption experiments were carried out at different temperatures (25,

190 30, 35, 40 and 45 ºC, respectively). GAC-0 was also subjected to the same experiments.

191 The SOC results presented in this study are the geometric mean of the SOC from three

192 replicates of a GAC sample, under the same temperature. Depending on the

193 temperature, not all the retained gaseous compounds will migrate to the gas phase, but

194 only those that are desorbed at the proposed temperatures (Martin et al., 2010).

195 Dynamic olfactometry was the method used to quantify the odor concentration (OC,

196 ou_E/m^3), which is necessary to calculate the SOC at the above mentioned temperatures.

197 All odor concentration data are expressed in accordance with the reference conditions

198 described in standard EN 13725 (2003) (i.e. 20 ºC, 101.3 kPa on a wet basis).

199 According to the European standard, all gaseous samples were analyzed within 30 h.

200 However, in order to minimize the permeation and/or adsorption of odorants through/on

201 the sampling bag walls, gaseous samples were analyzed within 6 h, as proposes the

202 guideline VDI 3880 (2011). Permeability and adsorption effects for odorants (such as

203 volatile sulfur compounds) in Nalophan® sampling bags were studied by several

204 authors, who demonstrated the influence of storage time on the above mentioned effects

205 (Kasper et al., 2018; Le et al., 2015; Toledo et al., 2019a). A TO8 olfactometer based on

206 the "Yes/No" method developed by Olfasense GmbH was used to determine the OC.

207 The panelist group consisted of 4 people who were selected based on their sensitivity to

208 the n-butanol reference gas as described in the above European standard. The individual

209 sensitivities of the panelists are within the range 20-80 ppb_v established by EN 13725

210 (2003), these being 49, 52, 62 and 68 ppb_v of n-butanol. The odor concentration was

211 calculated as the geometric mean of the odor threshold values of each panelist

212 multiplied by the square root of the dilution factor, which is 2 (Jiang et al., 2006).

213 *2.3.4. Quantification of volatile organic compounds*

214 A thermal desorption unit coupled with gas chromatography/mass spectrometry (TD-
215 GC/MS) was used to quantify the VOCs retained by the GAC samples, which were
216 grouped into families of odoriferous compounds. The methodology for this analysis is
217 described in the following sections.

218 *2.3.4.1. Preparation of blank samples and sampling*

219 A total of 44.5 mg of each GAC sample (GAC-0, GAC-1, GAC-2, GAC-3 and GAC-4)
220 was weighed and placed in individual microchambers at 40 ℃. Fifteen minutes after
221 placing the samples in the microchambers (equilibrium time), individual, freshly
222 cleaned adsorption tubes (TenaxTA/Carbograph5, Markes International, UK) were
223 inserted in the lid of each microchamber with an adjusted dynamic flow of 50 mL/min
224 (flow coming from the emitted headspace by the sample). After 30 minutes (sampling
225 time), the tubes on the lid of each microchamber were removed and inserted in the TD-
226 GC/MS system to perform the chromatographic analyses.

227 With respect to the preparation of the blank samples, the microchambers were set to
228 40 ℃ and a blank, freshly cleaned adsorption tube was inserted in the lid of each
229 microchamber under the same sampling conditions (30 min, 50 mL/min). These tubes
230 constitute the blank subtracted from each sample according to the microchamber used.

231 *2.3.4.2. Chromatographic analysis*

232 After collecting the VOCs in the adsorption tubes, they were inserted in the TD-GC/MS
233 system. As described above, the instrumentation system consisted of a thermal
234 desorption unit (Unity2-xr Markes International, UK), a gas chromatograph (GC)
235 (TRACE 1310, Thermo Fisher Scientific) and a mass spectrometer (MS) (ISQ 7000,
236 Thermo Fisher Scientific).

237   The VOCs were then removed from the tubes by thermal desorption (280–330 ℃) and

238   captured in a cold trap at low temperature (0–10°C) by thermoelectric cooling.

239   Subsequently, the cold trap was heated to 300–350°C according to a programmed and

240   optimized temperature profile to release all the VOCs into the GC column inlet through

241   a transfer line for their subsequent chromatographic separation. At the end of the GC

242   column, the separated compounds reach the MS with different (retention) times

243   (expressed in minutes), where they are fragmented and subsequently identified by the

244   NIST 2017 spectra database based on the fragmentation patterns of each molecule.

245   The GC system was equipped with the mid polar TG-624 column (60 m; 0.25 mm; 1.5

246   µm; Thermo Fisher Scientific). Temperature program of GC/MS analysis: initial oven

247   temperature 40 ℃, held for 5 min, ramped to 235 ℃ at 5 ℃/min, held for 7 min. Carrier

248   gas (He) was operated at 1.6 mL/min. Mass spectral detection was in electron impact

249   mode at 70 eV ionization energy. The m/z range was 35-350 (in "SCAN" mode). The

250   temperature of ion source was 230 ℃.

251   *2.3.4.3. Quantification*

252   Signals registered as (chromatographic) peaks were quantified by comparing their size

253   (area under curve) with the obtained area of a known amount (ng) of a reference

254   substance (Toluene-d8), which was adsorbed (by direct injection using a syringe) in an

255   additional clean tube. The peak produced by the Toluene-d8 was used as a reference

256   peak to quantify all peaks obtained in the sample analysis and served as an estimation of

257   a more accurate quantification based on calibration curves for each compound detected

258   in the samples. This method based on Toluene-d8 is known as semiquantitative

259   quantification.

260   *2.3.4.4. Quality parameters of the method*

261   Detection limits depend on the chemical nature of the compound and the sampling and

262   instrumental method used. As a general approach, this TD-GC/MS system can detect

263   substances from 0.01 to 1 ng. Depending on the sampling method used, these values can

264   be equivalent to 0.1 and 0.5 $\mu g/m^3$, respectively. The relative standard deviation (RSD)

265   of the values obtained by this method is below 10%.

266   Chemical identifications were obtained by GC-Analyzer software which compares all

267   detected fragment ions to allow the detection of very small differences either free from

268   interferences or buried under large peaks. Additionally, all identified peaks were

269   confirmed by the retention index, according to an own database. In complex cases

270   (low/saturated or overlapped signals), manual checking was performed and comparison

271   with our own database was also used. The compounds reported in this study were

272   identified with a certainty higher than 80%, most of them over 90%. Peaks identified

273   with a certainty below 80% were classified as an "unknown" group and their

274   concentrations were added up. Additionally, values below 0.1 $\mu g/m^3$ were included in

275   this group.

276   *2.3.5. H_2S and SO_2 quantification*

277   Other compounds of interest, such as hydrogen sulfide and sulfur dioxide, are too

278   volatile to be retained by the adsorption tubes. For this reason, these volatile sulfur

279   compounds were quantified using a fully automatic isothermal gas chromatograph

280   (Chroma S) coupled to a flame photometric detector (GC/FPD) developed by

281   Chromatotec. This equipment is adequate for the analysis of sulfur compounds and has

282   been described by Toledo et al. (2019a). Its detection limit is 7 ppb_v for both H_2S and

283   SO_2. To perform the analysis, 0.5 g of each GAC were placed in 4-L Nalophan®

284   sampling bags at 40 ℃ and maintained in isothermal conditions for 24 h. The bags had

285   been previously filled with clean, filtered air. One bag was prepared for each replicate,

286   each of which was analyzed in duplicate.

287   *2.3.6. Chemical contribution determination*

288   The chemical contribution (PC_i; Wu et al., 2017) of the chemical families detected by

289   TD-GC/MS indicates their relative concentration with respect to the total chemical

290   concentration. PC_i (%) was calculated as follows:

291    $$PC_i\,(\%) = \frac{\sum C_i}{C_t} * 100 \qquad\qquad (1)$$

292   where $\sum C_i$ is the cumulative concentration of a specific chemical family ($\mu g/m^3$) and C_t

293   is the total chemical concentration ($\mu g/m^3$).

294   *2.3.7. Odor activity values and odor contribution calculation*

295   It is well established in the literature (Rincón et al., 2019; Schiavon et al., 2017; Zhu et

296   al., 2016) that the odor activity value (OAV) is the ratio of the chemical concentration

297   of a single compound to its odor detection threshold (ODT). OAV is a dimensionless

298   parameter that has been widely employed to determine the odorous potential of each

299   compound contained in an odorous sample (Laor et al., 2014). In this work, OAV_i

300   represents the odorous potential of each chemical family and was calculated as follows:

301    $$OAV_i = \frac{\sum C_i}{ODT_i} \qquad\qquad (2)$$

302   where $\sum C_i$ is the cumulative concentration of a specific chemical family ($\mu g/m^3$) and

303   ODT_i is the geometric mean of the odor detection thresholds ($\mu g/m^3$) of the compounds

304   included in that specific chemical family. Of the ODTs used, 94% were reported by

305   Nagata (2003), while the remaining 6% were documented in Van Gemert (2011).

306   To determine the odor contribution (PO$_i$; Wu et al., 2017) of a chemical family, it is

307   useful to calculate OAV$_i$, as this value indicates the relative importance of each

308   chemical family with respect to the global olfactory perception. In this context, PO$_i$ (%)

309   was calculated as follows:

310    $$PO_i\ (\%) = \frac{OAV_i}{SOAV} * 100 \tag{3}$$

311   where OAV_i is the odor activity value of a specific chemical family (calculated by Eq. 2)

312   and $SOAV$ is the sum of all OAV$_i$ (i.e. $SOAV = \sum OAV_i$).

313   Given the above, it is important to mention that odor monitoring based on OAVs

314   presents two limitations: 1) the considerable variability among ODTs found in the

315   literature and within the same chemical family, and 2) the omission of possible

316   interactions among odorants which may produce synergistic, antagonistic or even

317   neutralizing effect when perceiving odorous gases (Parker et al., 2012; Wu et al., 2015).

318   **3. Results and discussion**

319   *3.1. GAC composition, surface functional groups and pH*

320   Pristine coconut-based GACs adsorb VOCs, but they have a relatively low capacity to

321   adsorb inorganic H$_2$S (Water Environment Federation, 2017). In order to neutralize this

322   acid and malodorous gas, WWTPs typically use activated carbons impregnated with

323   alkali substances, such as NaOH or KOH. The use of NaOH or KOH for the GAC

324   impregnation does not affect its adsorbing properties (Martin et al., 2010). In this sense,

325   the XRF results (Table 2) show the presence of Na or K in the GACs, which comes

326   from the alkaline impregnating agents. It is clear from this analysis that GAC-1, GAC-3

327   and GAC-4 were impregnated with NaOH, since high values of Na (%) can be

328   observed, while GAC-2 was impregnated with KOH. The elemental sulfur content (%)

329   was also analyzed. It is worth noting that GAC-1 presented the highest relative content

330   of S, followed by GAC-2, GAC-4 and GAC-3, the latter two with very low sulfur

331   values. The high presence of this element, mainly in GAC-1 and GAC-2, suggests a

332   higher retention of H_2S (in terms of chemisorption) in the early stages of the wastewater

333   treatment process (i.e. in the pretreatment). However, this does not occur with the

334   activated carbons from the sludge line deodorization (GAC-3 and GAC-4), where H_2S

335   is removed by the action of $FeCl_3$. Therefore, it could justify the low sulfur content in

336   both GAC-3 and GAC-4.

337   With regard to surface functional groups, and considering that GAC-0 was impregnated

338   with alkaline solution (NaOH or KOH), the presence of basic groups in the GAC

339   samples would be logical. Table 2 shows the presence of these groups in both GAC-3

340   and GAC-4. Nevertheless, both GAC-1 and GAC-2 have surface acidic groups. This

341   indicates that a large amount of acid compounds were chemically adsorbed during

342   deodorization at the wastewater pretreatment stage. In these carbons, the neutralization

343   reaction was so effective that the retention of acid compounds exhausted the basic

344   groups of GAC-0 and reversed their basic pH of 9.6 to acidic pH values (Fig. 2). In

345   addition, a higher content of surface acidic groups can be observed in GAC-1, which is

346   related to a greater adsorption of acid compounds with respect to GAC-2. This is also

347   observed in Fig. 2, which shows a lower (more acidic) pH for GAC-1 (pH = 4.1). This

348   is due to the fact that different circumstances coexist at the pretreatment header (GAC-

349   1), such as the high organic matter and nutrients load and the high presence of

350   microorganisms and anaerobic conditions, both of which entail a higher emission of

351   acid compounds (especially H_2S) compared to the rest of the WWTP operations (Jiang

352   et al., 2017).

353 Finally, in the case of GAC-3 and GAC-4, the pH values are basic and very similar to

354 the pH of GAC-0. Therefore, it could be said that the gaseous compounds, which are

355 emitted in the operations related to GAC-3 and GAC-4 (sludge thickening and sludge

356 dehydration, respectively), were mainly retained by means of physical adsorption

357 (physisorption) and/or the adsorption capacity of the bed was not exhausted before

358 replacement. Therefore, the neutralization process was minimal in both GAC-3 and

359 GAC-4.

360 *3.2. Conductivity, TOC and TN_s*

361 Conductivity values provide an approximate idea of the amount of gaseous compounds

362 retained in GAC samples, since the water extracts some of these compounds, which

363 remain in solution as ions. As can be observed in Fig. 2, GAC-1 presents the highest

364 conductivity value ($\approx$ 6 mS/cm), meaning that a greater quantity of ionic compounds

365 was retained in the adsorbent. This reaffirms that the emission of odoriferous sulfur

366 compounds (which have an ionic character) is greater at the pretreatment header.

367 Furthermore, this is related to the percentage of sulfur retained by GAC-1, which was

368 far higher than any of the other GACs (Table 2). Considering these latter carbons, an

369 increase in conductivity was detected in all cases with respect to GAC-0, thus indicating

370 that all of them retained (ionic) compounds during use.

371 TOC and TN_s refer to the fraction of organic and nitrogen compounds, respectively,

372 which have been solubilized in water during the aqueous extract. Regarding both

373 physico-chemical variables (Fig. 2), GAC-0 presents the lowest concentrations since

374 this carbon was not used in any adsorption process, and the values are due to the

375 composition of the pristine carbon itself. Therefore, the differences in TOC and TN_s

376 from these minimum values are a consequence of the adsorption of compounds by the

377 different GAC WWTP operations.

378 On the one hand, as regards TN_s, higher values were observed in the wastewater line

379 deodorization GACs than in the sludge line GACs, highlighting TN_s related to GAC-2

380 (1.09 mg/g GAC). According to Nguyen et al. (2019), the emission of nitrogen

381 compounds (especially NH_3) is greater in aerobic conditions (such as those taking place

382 in the sand and fat removal) due to the ammonification and nitrification reactions

383 carried out by ammonifying and nitrifying bacteria, respectively. In addition,

384 wastewater has a long residence time at this step of the WWTP. In contrast, anaerobic

385 conditions predominate in the pretreatment header due to the high content of organic

386 matter and microorganisms, which cause the dissolved oxygen to be consumed quickly.

387 Despite this, due to the high content of nutrients in the header, among them nitrogen,

388 they can be transferred from the liquid phase to the gas phase, thus explaining the high

389 value of TN_s in GAC-1 (0.97 mg/g GAC). Regarding GAC-3 and GAC-4, low TOC and

390 TN_s values were observed, especially in GAC-4. This is because GAC-4 was used in the

391 deodorization of the anaerobically treated sludge dewatering. As a consequence of this

392 operation, the microbial activity is considerably reduced (Nguyen et al., 2019) and the

393 emission of nitrogen compounds is therefore lower.

394 Moreover, with respect to TOC, GAC-4 is also the adsorbent with the lowest value

395 (0.46 mg/g GAC). This is due to two reasons: i) the reduction of microbial activity in

396 the sludge dehydration step and ii) the reduction of biodegradable compounds in

397 dehydrated sludge as a consequence of the previous anaerobic digestion carried out at

398 the WWTP. Both processes reduce the typical odor emissions derived from sludge

399 treatment (Orzi et al., 2015) and, consequently, the presence of TOC in GAC-4. In the

17

400   case of GAC-1, GAC-2 and GAC-3, higher and similar values can be observed in Fig. 2

401   (0.90–1.00 mg/g GAC) because of the higher organic load of the wastewater.

402   *3.3. Specific odor concentration and quantified odorous families*

403   In addition to the evaluation of the physico-chemical properties of the used GACs, their

404   removed specific odor concentrations (SOCs) and the adsorbed gaseous families were

405   studied.

406   It is well known that the odor concentration increases with increasing temperature

407   (Toledo et al., 2019b; Wu et al., 2018). In the present study, SOC ($ou_E/m^3 \cdot g$ GAC)

408   refers to the retained odor concentration per mass of adsorbent and the variation in SOC

409   with temperature is shown in Fig. 3. As can be observed in the figure, SOC values

410   increase with temperature up to 40 ℃ (especially in GAC-1 and GAC-2) due to the

411   greater desorption of retained compounds compared to lower temperatures. For this

412   reason, a temperature of 40 ℃ was selected as the limiting temperature to study the

413   desorbed compounds in the chromatographic analyses. In addition, a temperature of 40

414   ℃ is reached in summer in the province of Seville (location of the WWTP), this being

415   the most unfavorable situation of those studied in terms of odor nuisance. On this basis,

416   the control of operational temperatures in the different stages of wastewater treatment

417   should be essential, especially in the sludge dehydration room if this waste comes from

418   a mesophilic anaerobic digestion, as occurs in the studied WWTP.

419   It is also important to note that the removed specific odor concentration followed a

420   descending order of $SOC_{GAC-1} > SOC_{GAC-2} > SOC_{GAC-4} > SOC_{GAC-3} > SOC_{GAC-0}$. This

421   could suggest that the odor emissions were more significant in the first steps of the

422   integral wastewater treatment (especially at the pretreatment header), which is line with

423   the studies of Lebrero et al. (2011) and Gebicki et al. (2016). In order to clarify this

424   issue, it is necessary to examine the results of the TD-GC/MS and GC/FPD analyses.

425   Quantified volatile compounds (Table S1, Supplementary Material) are grouped into 14

426   gaseous families, which are shown in Table 3. Odor emissions from WWTPs often

427   contain these families (Fisher et al., 2018; Lebrero et al., 2011). It is important to point

428   out that ammonia was not quantified due to the limitations of the techniques used.

429   Therefore, the amount of odorants retained was underestimated for the nitrogen-

430   containing compounds family, since the emission of ammonia is common in WWTPs

431   (Lebrero et al., 2011). Nevertheless, nitrogenous compounds are not major sources of

432   WWTP odor due to the higher Henry's constants and higher ODTs with respect to other

433   chemicals, such as sulfur compounds (Jiang et al., 2017). The major families retained in

434   the GACs are analyzed in what follows.

435   • In GAC-1: terpenes, aliphatic hydrocarbons, aromatic compounds and sulfur-

436   containing compounds were the predominant families. Terpenes are the family

437   that most saturated this adsorbent and are possibly related to household

438   discharges, because they are very common odoriferous compounds in cleaning

439   agents and cosmetics (Lehtinen and Veijanen, 2011). Camphene (14.383 µg/g

440   GAC) and d-limonene (8.751 µg/g GAC) together accounted for almost 60% of

441   the total adsorbed terpenes. It is also important to highlight that GAC-1 was the

442   carbon that retained a greater total amount of odorants.

443   • In GAC-2: sulfur-containing compounds and terpenes.

444   • In both GAC-3 and GAC-4, sulfur-containing compounds and, to a lesser extent,

445   aromatic compounds predominated.

446   As can be seen in Table 3, there was a higher content of sulfur-containing compounds in

447   all the carbons. According to Choi et al. (2012), the main chemical reactions which

448   produce these compounds in wastewater are: (i) the reduction of sulfate to sulfide

449   involving sulfate-reducing bacteria, (ii) the degradation of amino acids which contains

450   sulfur, (iii) the methylation of methyl mercaptan by hydrogen sulfide and (iv) the

451   generation of dimethyl sulfide by means of the oxidation of methyl mercaptan. In

452   addition, it is important to note that H_2S, which is reported in the literature as the main

453   odoriferous compound in WWTPs (Talaiekhozani et al., 2016), was only present in

454   GAC-1 (5.631 µg/g GAC) and GAC-2 (3.977 µg/g GAC) since this odorant was

455   precipitated by the action of $FeCl_3$ in the sludge line operations. The presence of H_2S

456   explains the lower pH values (Fig. 2) as well as the higher elemental sulfur values

457   (Table 2) in both GAC-1 and GAC-2 with respect to the sludge line GACs due to the

458   retention of the compound in terms of chemisorption. Therefore, it can be said that the

459   combination of analytical techniques facilitates a better understanding of the physico-

460   chemical processes that took place in each of the WWTP odor adsorption lines.

461   *3.4. Chemical and odor contribution of the gaseous families*

462   Taking into account the odor contribution of the gaseous families (PO_i), Fig. 4

463   illustrates the results for this variable as well as the chemical contribution of each (PC_i)

464   for purposes of comparison. As can be seen in the figure, the PO_i trend was different

465   from the PC_i trend, especially in GAC-1 and GAC-2.

466   More specifically, in the case of the wastewater line GACs, Fig. 4(a) shows a very

467   heterogeneous PC_i compared to the sludge line GACs, where sulfur compounds

468   predominated (other than H_2S). It is also interesting that PC_i of aromatic compounds

469   barely changed as the wastewater treatment process progressed. According to Maier

470   (2019), this could be linked to the low water solubility of aromatic compounds, which

471   results in slow biodegradation rates, thus hindering their bioelimination from

472   wastewater and, consequently, from air (due to liquid-gas transfer).

473   Additionally, Fig. 4(b) shows that sulfur-containing compounds were the major odor

474   contributors (PO_i = 61–97%) for all GACs due to their very low ODTs (Byliński et al.,

475   2019a). Taking into account the wastewater line GACs, hydrogen sulfide was by far the

476   major odor contributor. However, in the case of the sludge line GACs, even when H_2S

477   was eliminated by the action of $FeCl_3$, other volatile sulfur compounds continued to

478   make a significant contribution to the total odor emitted from the sludge handling units.

479   These include the organic-reduced sulfur compounds, mainly dimethyl disulfide

480   (DMDS), and to a lesser extent, dimethyl trisulfide (DMTS) and dimethyl sulfide

481   (DMS), which are mainly produced by the anaerobic degradation of organic matter

482   present in wastewater (Water Environment Federation, 2017). Therefore, the removal of

483   hydrogen sulfide alone from sewage results in a marginal reduction in the odor

484   contribution if volatile organic sulfur compounds predominate. Finally, it is also

485   important to note the odor contribution of aldehydes in GAC-1 ($PO_i \approx 17\%$). These

486   compounds are most likely the result of the anaerobic degradation of organic matter

487   (Lehtinen, 2013) and have also been reported as key odorants in WWTPs emissions

488   (Jiang et al., 2017).

489   *3.5. Textural properties*

490   According to the previous analysis, a higher amount and variety of gaseous compounds

491   were emitted in the first steps of the integral wastewater treatment, as can be seen in

492   Table 3 and Fig. 4(a), respectively. This should cause a greater change in the textural

493   properties of the GAC samples from the wastewater line deodorization (GAC-1 and

494   GAC-2). In this context, Table 4 shows very low values for both the free surface area

495   (specific surface area, S_{BET}, and micropore area, S_{micro}) and the free pore volume (total

496   pore volume, V_t, and micropore volume, V_{micro}) for the above mentioned carbons in

497   comparison with pristine GAC-0 and the sludge line GACs (GAC-3 and GAC-4). It is

498   also important to highlight the relevant role the micropores of the adsorbent beds had in

499   deodorization, which were practically exhausted in GAC-1. Microporosity depletion

500   caused an opposite effect in the value of the average pore width (D_{pore}), leading to an

501   increase from 2.26 nm in GAC-0 to 4.54 and 2.48 nm in GAC-1 and GAC-2,

502   respectively. These values confirm the textural change of GAC-0, which changed from

503   a dual micro-mesoporous nature to a completely mesoporous character after the

504   retention of the odoriferous compounds. With respect to the sludge line GACs, both the

505   surface area and pore volume values decreased only slightly with respect to GAC-0 due

506   to the lower intensity of the gaseous emissions in the sludge line operations, which was

507   in turn related to the gradual decrease in the organic load as the treatment process

508   progressed in the WWTP. Furthermore, the average pore width of both GAC-3 and

509   GAC-4 was only slightly modified compared to GAC-0. As shown in Table 4, there was

510   a slight increase in this variable due to the partial loss of microporosity and the

511   consequent increase in mesoporosity.

512   *3.6. Relationships between variables: TC, SOC and V_{micro}*

513   This last section provides an overview of the integral evaluation of the deodorization

514   system of the urban WWTP in terms of total concentration of desorbed gaseous

515   compounds (TC, µg/g GAC), free micropore volume (V_{micro}, cm^3/g) and removed

516   specific odor concentration (SOC, ou$_E$/m$^3\cdot$g GAC). As shown in Fig. 5, GAC-1 is the

517   adsorbent that retained the highest TC ($\approx$ 150 µg/g GAC), while GAC-3 retained the

518   lowest ($\approx$ 30 µg/g GAC). Consequently, GAC-1 shows the lowest V_{micro} value, followed

22

519   (in ascending order) by GAC-2, GAC-4 and finally GAC-3. As mentioned, NH_3 was not

520   quantified, thus leading to an underestimation of TC. This is particularly noteworthy in

521   GAC-2, where a high retention of NH_3 was detected (Fig. 2 shows the highest TN_s for

522   GAC-2). Given this, GAC-2 was excluded from a simple linear regression model ($R^2 =$

523   0.9925) used to inversely correlate TC with V_{micro}. GAC-0 was excluded from the

524   model as it is the pristine sample.

525   Finally, the relationship between SOC and V_{micro} was also studied. Thus, without taking

526   into account GAC-0, and by means of a simple linear regression model ($R^2 = 0.9945$),

527   SOC was found to be inversely proportional to V_{micro} for the samples under study. This

528   means that the lower $V_{micro,}$ the higher SOC. For this reason, SOC might also be an

529   indicator of the GAC adsorption capacity loss in the WWTP.

530   These results show that a multi-technical study of the most important characteristics of

531   the adsorbent used in the urban WWTP contributes to a better understanding of the odor

532   removal process (through adsorption by GAC) in the different steps of the integral

533   wastewater treatment, as well as in possible operation strategies that optimize the

534   efficiency and usage time of GAC systems.

535   **4. Conclusions**

536   The main conclusions of this work are presented in what follows.

537   • In the urban WWTP under study, the wastewater line gaseous emissions were

538   found to be more significant than the sludge line emissions. Thus, GAC-1 and

539   GAC-2 showed a lower pH than GAC-3 and GAC-4, with the basic surface

540   groups being exhausted in the first adsorbents.

- In line with the above, odor emissions mainly affect the textural properties of the wastewater line GACs, since these materials have a higher amount (and variety) of retained odoriferous compounds (especially GAC-1). The retention of odorants is also important in the sludge line GACs and is mainly related to the physisorption of sulfur VOCs (especially DMDS). In addition, TC and V_{micro} have been inversely correlated using a simple linear regression model ($R^2 = 0.9925$).

- SOC provides an estimated view of the odor concentration emitted at the different odor sources considered and might also be an indicator of the GAC adsorption capacity loss. Thus, SOC and V_{micro} have also been inversely correlated ($R^2 = 0.9945$).

- Sulfur-containing compounds were the major odor contributors in all the odor sources (PO_i = 61-97%). However, H_2S cannot be considered as the major odorant in the WWTP, since the removal of this compound alone led to a marginal reduction in odor contribution.

Given the above, the multi-technical analysis carried out in this work could be useful for the optimal design of deodorization operations based on GAC, since it has shown that not all GAC beds have the same lifespan and that the quantification of H_2S alone is insufficient to determine their odor removal efficiencies. In this sense, the dynamic olfactometric and/or the quantification of the GAC textural properties (S_{BET} and V_{micro}) provide better evidence of the saturation level of the GAC beds, which in turn may result in optimizing the use of the adsorbent material, operating costs and ambient air quality. With regard to the latter, analyses of this kind would be beneficial for improving occupational health within WWTPs and reducing the odor impact in nearby populations.

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735

736 **Figure captions**

737 Figure 1. Schematic diagram of the WWTP

738 Figure 2. Physico-chemical characterization of the GAC samples: soluble total organic

739 carbon (TOC), soluble total nitrogen (TN_s), pH and conductivity

740 Figure 3. Variation in the removed specific odor concentration (SOC) with temperature

741 Figure 4. Comparison between chemical contribution (a) and odor contribution (b) of

742 the gaseous families

743 Figure 5. Relationships between variables: total concentration of desorbed gaseous

744 compounds (TC), removed specific odor concentration (SOC) and free micropore

745 volume (V_{micro}). Legend: gray, GAC-0; black, GAC-1; red, GAC-2; green, GAC-3;
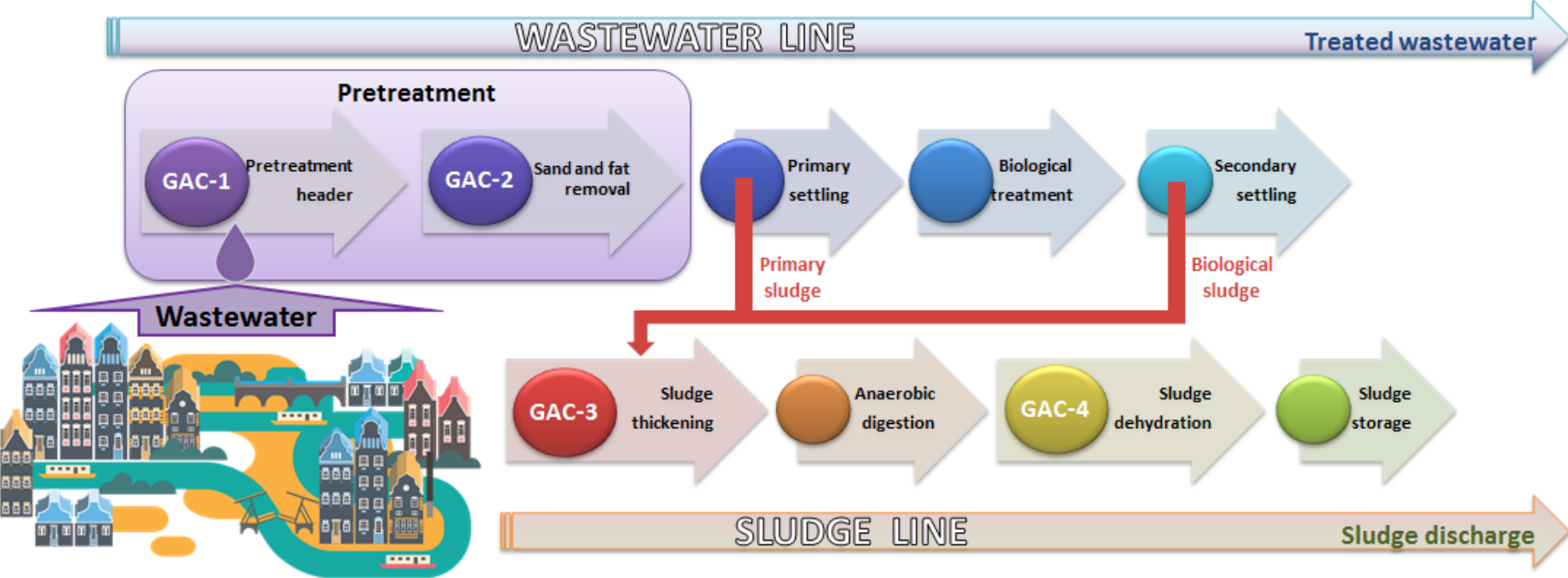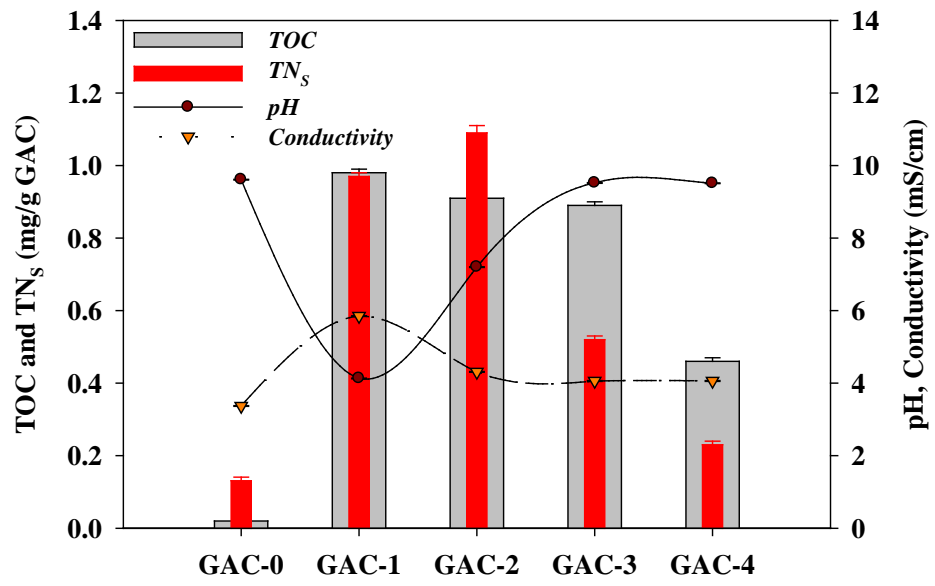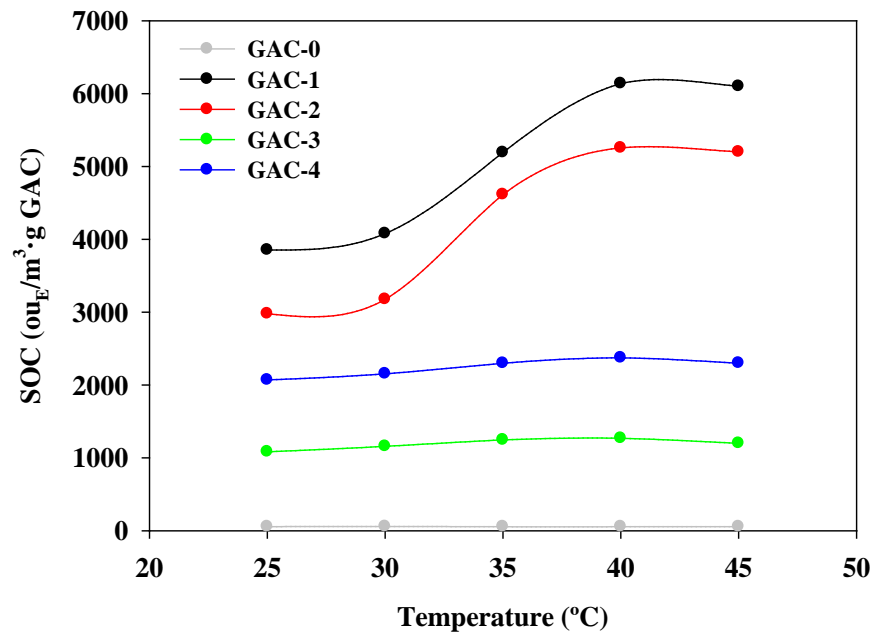
746 blue, GAC-4.

Figure 1.

Figure 2.

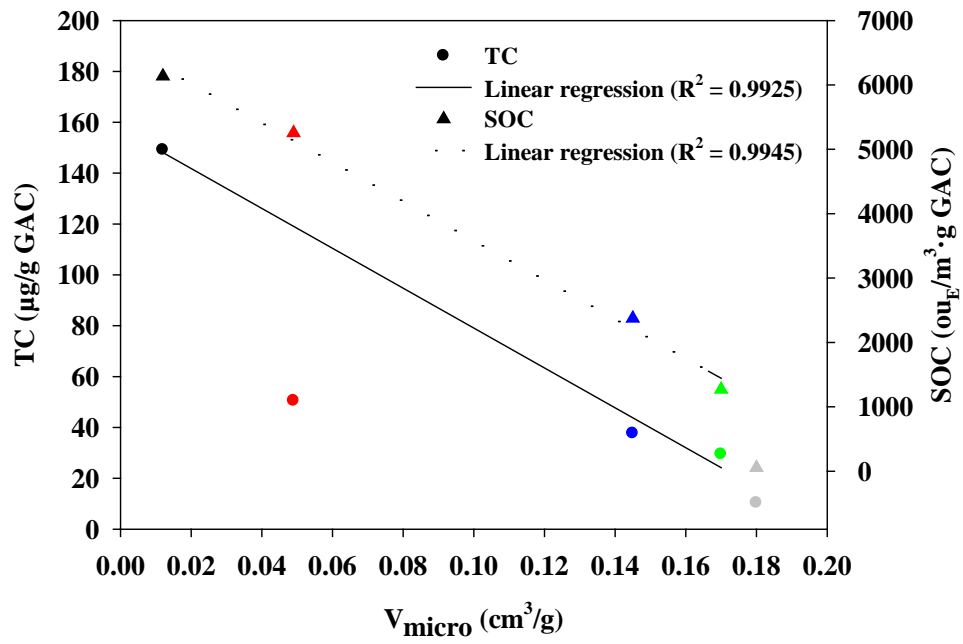**Figure 3.**

Figure 4.

Figure 5.

Table 1. *Origin of GAC samples and description of deodorization towers.*

GAC samples (acronym)	Origin	Operation description	Number of deodorization towers	Tower height (m)	Tower diameter (m)	Flow speed (m/s per tower)	Treated air flow (Nm³/h per tower)	Amount of GAC (kg per tower)	Number of GAC beds (per tower)	Bed height (m)	Bed capacity (m³)
Sample 1 (GAC-1)	Pretreatment header	Roughing operations, water elevation using worm screws and screening	1	3.60	3.00	2829	20,000	3900	2	0.50	3.53
Sample 2 (GAC-2)	Pretreatment	Sand and fat removal	2	3.80	3.50	2079	20,000	5300	2	0.50	4.81
Sample 3 (GAC-3)	Sludge thickening	Gravity thickening of sludge from primary treatment and flotation thickening of sludge from biological treatment	2	2.23	2.25	1006	4,000	1325	1	0.60	2.39
Sample 4 (GAC-4)	Sludge dehydration	Dehydration of the sludge from anaerobic digestion	1	1.65	1.40	1299	2,000	500	1	0.60	0.92

Table 2. *Characterization of GAC samples: acidic and basic surface groups and elemental composition of Na, K and S.*

GAC samples	Boehm method		X-ray fluorescence (XRF)		
	Basic surface groups [OH⁻] (mmol/g GAC)	Acidic surface groups [H⁺] (mmol/g GAC)	Na	K (% by weight)	S
GAC-1	-	2.73 ± 0.38	2.79 ± 0.05	0.05 ± 0.01	15.25 ± 1.02
GAC-2	-	1.89 ± 0.28	0.20 ± 0.01	2.35 ± 0.08	5.09 ± 0.14
GAC-3	2.31 ± 0.06	-	3.95 ± 0.07	0.07 ± 0.01	0.50 ± 0.02
GAC-4	1.88 ± 0.25	-	3.75 ± 0.11	0.07 ± 0.01	0.57 ± 0.02

Table 3. *Concentration of families of gaseous compounds identified in the GAC samples.*

Families of compounds	Concentration (µg/g GAC) (dry basis)				
	GAC-0	GAC-1	GAC-2	GAC-3	GAC-4
Alcohols	0.230	1.513	0.735	0.150	0.512
Aldehydes	-	0.845	0.056	-	-
Aliphatic hydrocarbons	0.075	23.808	2.047	1.992	0.354
Aromatic compounds	-	23.001	9.384	6.177	9.143
Cyclic hydrocarbons	0.380	10.728	5.390	0.189	0.700
Esters	-	0.560	0.159	-	0.123
Ethers	0.108	0.562	0.160	0.032	0.070
Furans	0.588	-	0.010	0.133	0.135
Halogen-containing compounds	-	4.860	1.443	0.061	0.091
Ketones	-	5.213	1.483	-	0.091
Nitrogen-containing compounds	2.507	0.198	0.058	-	-
Organic acids	2.254	0.486	0.235	0.049	0.073
Sulfur-containing compounds	-	19.911	14.500	19.264	24.612
Terpenes	0.111	39.084	13.463	1.012	1.557
"Unknown"	3.061	18.210	1.351	0.309	0.135
Total concentration (TC)	9.314	148.978	50.475	29.368	37.596

Limit of detection (LOD): 0.0058 (µg/g GAC)

Table 4. *Textural properties of GAC samples.*

GAC samples	S_{BET} (m²/g)	S_{micro} (m²/g)	V_t (cm³/g)	V_{micro} (cm³/g)	D_{pore} (nm)
GAC-0	406	236	0.229	0.180	2.26
GAC-1	36	-	0.041	0.012	4.54
GAC-2	156	63	0.097	0.049	2.48
GAC-3	336	229	0.191	0.170	2.28
GAC-4	328	169	0.191	0.145	2.33

S_{BET}, specific surface area; S_{micro}, micropore area; V_t, total pore volume; V_{micro}, micropore volume; D_{pore}, average pore width