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1 Sewage Sludge Ash-derived materials for H₂S 2 removal from a landfill biogas

3
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9 10 **Abstract**

11 H₂S removal is a key step for biogas cleaning because this component can lead to premature corrosion
12 of the equipment and its cleaning has a significant cost. The aim of the present work was to assess the
13 use of sewage sludge derived ash (SSA)-materials for H₂S removal from a landfill biogas. SSA and
14 mixtures made with SSA, activated carbon (AC) and sand were tested for H₂S removal. The best
15 removal efficiency was obtained with the mixture 80%_m SSA and 20%_m AC, while SSA alone was
16 not a good adsorbent under tested experimental conditions. The materials characterization helped the
17 adsorption mechanism understanding. Indeed, results highlighted that SSA presence stabilizes the pH
18 on a basic range, favorable for H₂S dissociation into HS⁻ then its chemisorption. On the other hand,
19 with the microporosity of AC, the contact surface between H₂S and oxygen was sufficiently large for
20 chemisorption kinetics. It also appeared that the mixture with sand and AC adsorbs non selectively H₂S
21 but also other volatile organic pollutants present in biogas. Contrariwise, with SSA/AC mixtures, H₂S
22 seems to be selectively chemisorbed.

23 **Keywords:** Sewage sludge ash, Biogas, H₂S removal, adsorption

26 **1. Introduction**

27 Sewage sludge (SS) is a by-product of wastewater treatment. Its composition varies, as different
28 processing operations are available, according to the nature of pollutions. In order to facilitate its
29 deposit or valorization, this produced sludge has to be stabilized. Three methods are available:
30 thermal, chemical and biological stabilization (Gutiérrez Ortiz *et al.*, 2014). The chosen treatment and
31 stabilization conditions (temperature and gas nature for a thermal treatment for example) can affect
32 characteristics of the materials.

33

34 A European directive (200/60/EC) adopted on October 23rd 2000 defined sludge not as a waste
35 material but as a product of sewage treatment (European Parliament, Directive 2000/60/EC). The
36 conurbations must monitor and report sewage treatments and sludge disposal (Kacprzak *et al.*, 2017).
37 The European Parliament and Council Directive 2008/98/EC of November 19th 2008 states that a
38 priority in SS management is its preparation in order to reuse, recycle or recover it in another form
39 (European Parliament, Directive 2009/28/EC). In the next years, the amount of SS sent to landfills will
40 be restricted regarding orientations given by the current regulations. Incineration is a common option
41 for SS management to reduce its volume. Indeed, in European Union, approximatively 10 Mt dry mass
42 of SS is produced each year, of which 22% is incinerated (Lynn *et al.*, 2015). In order to save
43 resources and participate to circular economy, Sewage Sludge Ash (SSA) is partly recycled as a
44 building material such as cement or concrete mortars, as an inert material in replacement of sand or as
45 replacement of raw materials for light aggregates production (Lynn *et al.*, 2018).

46

47 On the other hand, another current issue is energy production and the limitation of CO₂ emissions.
48 Renewable energy development is therefore necessary. Biogas is a renewable gas obtained by the
49 anaerobic digestion of organic waste, such as SS. Biogas' advantages are its non-intermittence, the
50 possibility to produce it locally (and consequently less transport) and its different uses. Indeed, biogas
51 can be valorized for heat and power generation with a CHP unit, as a fuel for vehicles (compressed or
52 liquefied) and injected into the gas grid, for domestic or industrial use.

53

54 Biogas must be cleaned because it contains many pollutants, in particular hydrogen sulfide (H₂S). Its
55 concentration ranges from 10 to 10,000 ppm_v depending on the biogas origin. Currently, this pollutant
56 can be removed with biological treatment, by adsorption on iron oxides/hydroxides or on impregnated
57 activated carbon (Awe *et al.*, 2017). All these technologies have drawbacks and especially natural
58 resources depletion. It is the reason why the possibility of adsorbing H₂S on alternative materials is
59 studied Based on the literature, H₂S can be removed with mineral wool waste (Bergersen and
60 Haarstad, 2014), basic oxygen furnace slag (Sarperi *et al.*, 2014), alum sludge (Ren *et al.*, 2020),
61 municipal solid waste incineration bottom ash (del Valle-Zermeño *et al.*, 2015; Fontseré Obis *et al.*,
62 2017a) and also biochars (Shang *et al.*, 2013;2016; Bamdad *et al.*, 2018).

63

64 SS has been used as precursor for adsorbents production, after a pyrolysis (Bagreev *et al.*, 2001; Ros *et*
65 *al.*, 2006; Gutiérrez Ortiz *et al.*, 2014). This thermal treatment develops the material porosity, with
66 surface area going from 12 to 248 m²/g (Wallas *et al.*, 2014; Possa *et al.*, 2018). The pyrolyzed sludge
67 contains 50-70% organic matter and is also enriched in metals such as iron, zinc and aluminum (Ros *et*
68 *al.*, 2006). For H₂S removal, pyrolyzed sludge can also be impregnated with NaOH (Polruang *et al.*,
69 2017), with HCl (Possa *et al.*, 2018) or activated with CO₂ (Wallas *et al.*, 2014). Adsorption capacities
70 until 183 mg_{H₂S}/g_{DM} are obtained with pyrolyzed SS (Ros *et al.*, 2007). The adsorption results show
71 that the pyrolysis temperature has a significant influence on removal capacities, with an adsorption
72 capacity going from 14.9 to 82.6 mg_{H₂S}/g_{DM} for the same sludge pyrolyzed respectively at 600 and
73 950°C. However, most of these studies are realized with air or synthetic biogas and not with a real and
74 complex biogas. Furthermore, no study has been reported on the use of SSA for H₂S adsorption. The
75 main difference between SS biochars and SSA is the porosity, very low for SSA unlike the biochars'
76 one. Adsorption is a surface mechanism and can be limited by a low porosity.

77

78 Some studies deal with H₂S adsorption using formulated materials, associating an alternative material
79 and activated carbon (AC) in order to use its porosity. Florent *et al.* worked on materials made from
80 SS and AC pyrolyzed together at 600 or 800°C (Florent *et al.*, 2019). Mixtures containing 10 and 30%
81 of AC are three times more efficient for H₂S removal than the sludge pyrolyzed alone, with a final

82 adsorption capacity of 22 mg_{H₂S}/g. The authors indicate that the porosity contribution leads to a better
83 availability of catalytic centers linked with H₂S oxidation. Sioukri *et al.* (2005) observed an evolution
84 of the theoretical and real adsorption capacity from 30 to 80 mg_{H₂S}/g with a mixture SS/AC pyrolyzed
85 at 950°C. The developed pore system is used to store the oxidation products of H₂S removal.
86 Therefore, it seems interesting to add AC to SSA in order to obtain a good adsorbent for H₂S.

87

88 The objective of this work is to estimate the potential of SSA itself and SSA blended with AC as
89 adsorbent for H₂S removal from a real landfill biogas and to understand related adsorption
90 mechanisms.

91

92 **2. Materials and methods**

93 **2.1. Materials**

94 SSA was collected from a wastewater treatment plant situated in the southeast part of France. SSA
95 was obtained by combustion of urban SS (a mix of primary and secondary sludge) in a fluidized bed
96 furnace at 900°C and recovered from the fumes thanks to an electrostatic precipitator. SSA contains
97 30% SiO₂, 23% CaO, 16% P₂O₅, 10% Al₂O₃, and 7% Fe₂O₃ (low loss-on-ignition, 5%). The high
98 amount of phosphoric oxide can be explained by dephosphatation in wastewater treatment plant. No
99 pretreatments were realized on the ash due to its particle size (< 100 μm). AC used for adsorption tests
100 is the Pulsorb 208CP, produced by Chemviron, a Kuraray branch. It was obtained by coconut shells
101 carbonization, activated with vapor and ground in powder form. The supplier indicates a surface area
102 of 1200 m²/g. A sand was also used as an inert additive to AC compare to SSA for H₂S adsorption. It
103 is produced by Sibelco (ref. HN31) and composed of 98.9% of silica.

104

105 Primary test showed that the adsorption efficiency increases with humidity (result not shown here).
106 For adsorption experiment, SSA was humidified at 20%*m*. Distilled water was slowly added to the
107 raw material with a continuous stirring. Mixtures were realized by mixing SSA or sand with AC in
108 percentage of mass. The water contents of all mixtures were adjusted to 15-20% w/w which is

109 considered as optimal water contents for better H₂S adsorption according to the previous study
110 (Fontseré *et al.*, 2017b), highlighting water influence of H₂S adsorption.

111

112 Four different samples were prepared for adsorption test comparing: SSA alone, two mixtures of SSA
113 with AC (10%_m and 20%_m of AC) and a mixture of sand with 20%_m of AC. Subsequently, to lighten
114 the text, these studied samples will be respectively called: SL (SSA alone), SLA10 (SSA with 10%_m
115 of AC), SLA20 (SSA with 20%_m of AC) and SDA20 (sand with 20%_m of AC).

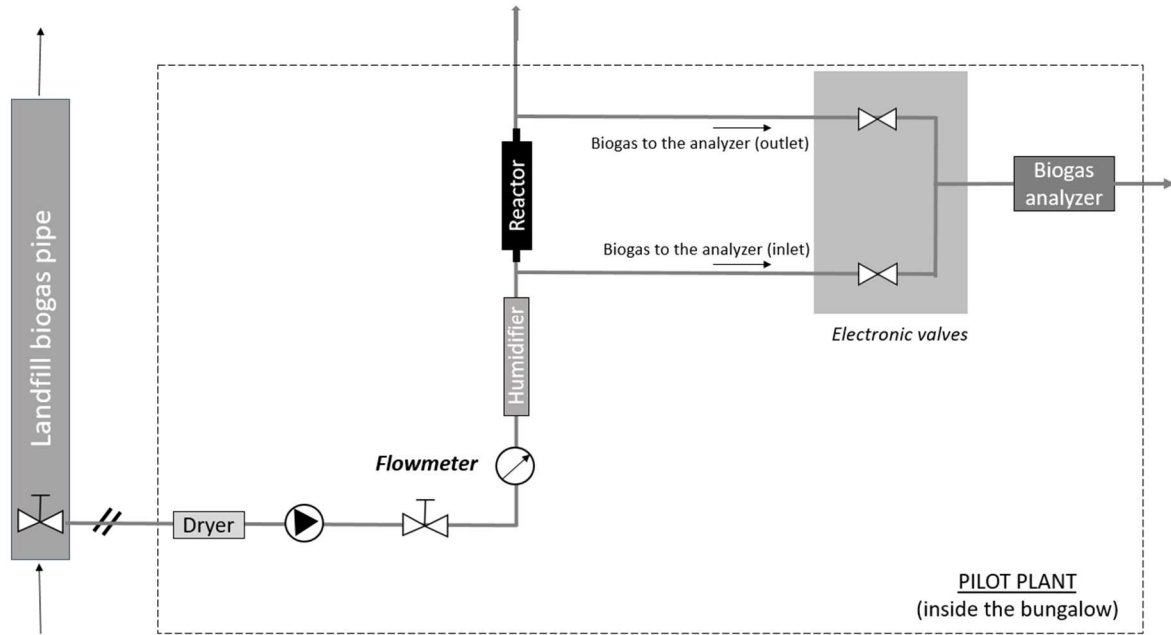
116

117 **2.2. Biogas adsorption tests**

118 The experimental set-up for biogas adsorption tests was described previously (Gasquet *et al.*, 2020)
119 and the diagram is presented on the Figure 1. To summarize, experiments were realized on a landfill,
120 using a real biogas. Consequently, the inlet biogas composition did not stay constant for all the tests.
121 The mean H₂S concentration ranged between 1415 to 1715 ppm_v, as observed in Table 1. Indeed,
122 depending on the grid management, some air can be introduced in the biogas and diluted it. Moreover,
123 for the same reason, H₂S concentration can reach 5000 ppm_v during a short period. These variations
124 may have an influence on the amount of H₂S captured and it is therefore important to consider it. The
125 tests were not realized simultaneously and the biogas mean temperature was around 21°C.

126

127 A reactor of 24.5 cm high and a diameter of 4 cm was used. The material volume was constant for all
128 experiments (251 cm³), with a fixed height in the reactor equal to 20 cm. This is the reason why the
129 mass of dry sample was different for each case, with different densities, from 0.9 for SL to 2.65 for
130 SDA20 (see Table 1). Hence, the AC mass was different for each test, with respectively 11.4, 21.9 and
131 44.9 g for SLA10, SLA20 and SDA20. The biogas flow was fixed at 1 L/min, using a Ritter
132 volumetric flowmeter. Residence time in the reactor was therefore equal to 15 seconds. Biogas
133 composition was analyzed with an infrared laser spectrometer called ProCeas. Biogas bubbles in a vial
134 containing water before the reactor to humidify it.



135

136

Figure 1 : Lab-scale adsorption pilot

137

138 In order to compare the materials, some parameters are calculated. First, H_2S_{passed} and $H_2S_{captured}$ are
 139 calculated as presented in equations (1) and (2), with $[H_2S]_{inlet}$ and $[H_2S]_{outlet}$ respectively the inlet and
 140 outlet H_2S concentration in g/m^3 . \dot{V} represents the gas flow in m^3/min . Mass adsorption capacity is
 141 obtained by dividing the H_2S amount removed by the dry mass of the adsorbent. The H_2S amount
 142 captured at which point the ratio $[H_2S]_{outlet}/[H_2S]_{inlet}$ is equal to 0.1 (10%) is also compared for the
 143 materials.

$$H_2S_{passed} = \int_0^t [H_2S]_{inlet}(t) \times \dot{V}(t) dt \quad (1)$$

$$H_2S_{captured} = \int_0^t ([H_2S]_{inlet}(t) - [H_2S]_{outlet}(t)) \times \dot{V}(t) dt \quad (2)$$

144

145

146 **Table 1: Summary of experimental conditions of adsorption tests for SSA derived materials**

Material	Duration (days)	Flow (L/min)	[H ₂ S] inlet (ppm _v)	Temperature (°C)	Masse of dry sample (g)
SL	7	1.05	1415 ± 605	20.3 ± 1.9	138.6
SLA10	10	0.97	1445 ± 255	20.1 ± 1.1	114.2
SLA20	8	1.03	1680 ± 780	21.0 ± 1.7	109.7
SDA20	7	0.95	1715 ± 825	21.0 ± 1.4	224.3

147

148 **2.3. Materials characterization**

149 To compare physicochemical characteristics between different materials but also to better understand
 150 H₂S adsorption mechanisms, following analyses were performed.

151

152 Water content was measured by drying the material at 105°C during 24 hours in a Memmert oven. All
 153 analyses were carried out in triplicate with 20-30 g of sample. Surface area and porous volume were
 154 measured by nitrogen adsorption at 77 K using ASAP 2020 device from Micromeritics. The surface
 155 area was evaluated with the Brunauer Emmett Teller (BET) model using the software MicroActive
 156 from Micromeritics. The porous volume was calculated with the Saius software from Micromeritics,
 157 applying the NLDFT model “Carbon 2D Heterogeneous Surface”. This method allows the
 158 characterization of the micro (< 2 nm) and mesoporosity (between 2 and 50 nm).

159

160 pH was measured with a calibrated pH-meter (Consort C3431) after 48 h leaching with distilled water,
 161 based on the ANC 14429 norm. CHNS composition was determined with a FlashEA 1112 Series
 162 analyzer from ThermoFischer. The major element (with a concentration higher than 10 g/kg)
 163 compositions were determined with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-
 164 OES, Thermo Fischer Icap 6500) after sample fusion with LiBO₂ followed by dissolution using HNO₃.

165

166 Raman spectroscopy was realized at room temperature under air with a Kaiser RXN1 and a Charged-
 167 Coupled Device of the same brand. Spectra were obtained with an excitation laser working at a
 168 wavelength of 785 nm. The acquisition spectral region goes from 100 to 3420 cm⁻¹ with a resolution of
 169 4 cm⁻¹. Pyrolysis with Gas Chromatography-Mass Spectroscopy (Pyro GC-MS) consists of an analysis

170 of the gaseous components produced during a flash pyrolysis, at 550°C. 1 to 2 mg of sample was
171 introduced in the pyrolyzer (EGA/Py-3030D model from Frontier Lab) at the desired temperature
172 under inert gas (He). The pyrolysis gas was drawn to the chromatography column (HP-5ms). After this
173 column, the mass spectrometer (simple quadrupole model 5977B from Agilent) detects the
174 components depending on the ratio mass to charge (m/z).

175

176 **3. Results**

177 *3.1. Comparison of H₂S removal efficiencies*

178 On the Figure 2, the evolution of the ratio $[\text{H}_2\text{S}]_{\text{outlet}}$ over $[\text{H}_2\text{S}]_{\text{inlet}}$ also called C/C₀ is observed as a
179 function of the time for the SL, SLA10, SLA20 and SDA20.

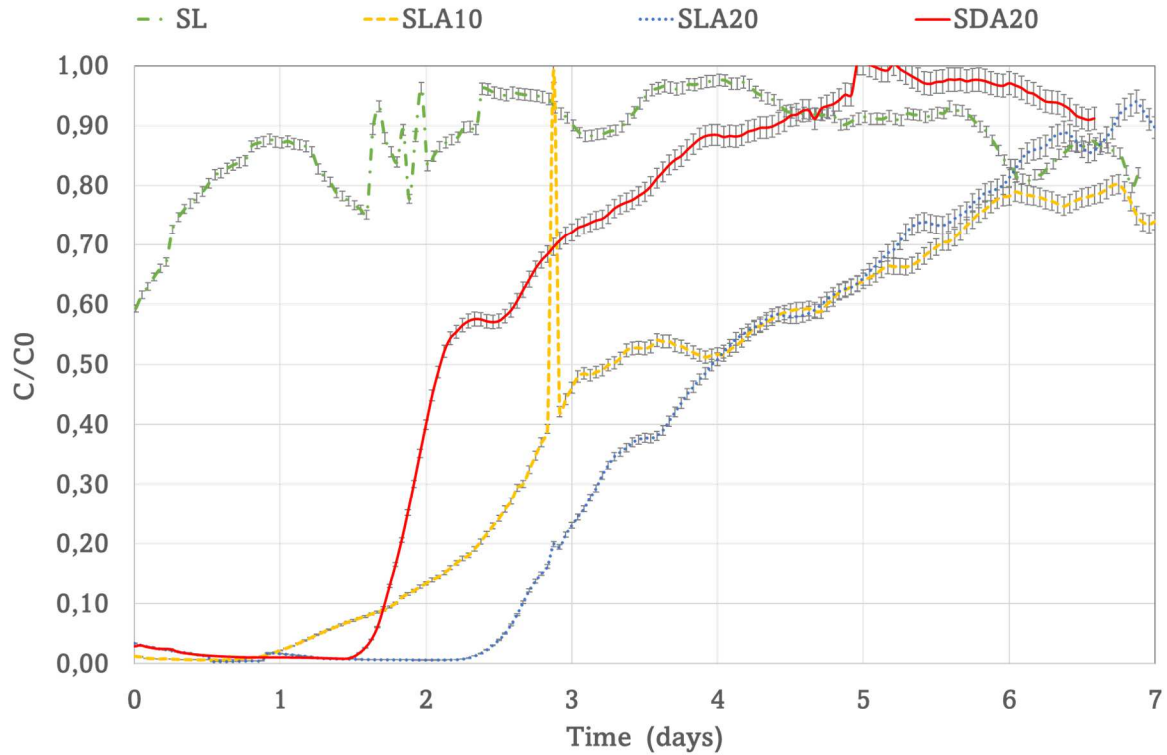
180

181 First, it appears that SL had quite different behaviors compared to other materials. The immediate
182 breakthrough shows that the adsorbent never removes all the H₂S from the biogas. More than 80% of
183 the inlet H₂S was found at the outlet of the reactor, around 1100 ppm_v. The ratio C/C₀ remained
184 constant during the entire test. Therefore, this material can remove a constant (low) amount of H₂S
185 during around one week. Adsorption mechanisms take place but not sufficiently to use SL as an
186 effective adsorbent for H₂S.

187

188 The three materials containing AC could remove all H₂S during the first day. The breakthrough was
189 first observed for SLA10 after one day, and then for SDA20 after 1.7 days. Finally the last
190 breakthrough was observed for SLA20 (2.7 days). The curve slope was not either the same, with a
191 steeper slope for SDA20. This material reached faster its total saturation. A peak was observed for
192 SLA10 at 2.8 days. It can be explained by a quick rise of H₂S inlet concentration (5000 ppm_v) due to
193 the landfill grid management. At this point, inlet H₂S amount was too high for materials to adsorb the
194 same H₂S fraction than the one adsorbed when H₂S inlet concentration was 1500 ppm_v. Finally, after 6
195 days, all materials removed less than 25% of the inlet H₂S.

196



197

198

Figure 2: Evolution of C/C_0 as a function of the time for SSA derived materials

199

200 The main adsorption results are summarized in Table 2. The total H_2S amounts passed and captured
 201 are presented. The ratio $H_2S_{\text{captured}}/H_2S_{\text{passed}}$ is also calculated. It evolved from 0.14 for SL to 0.56 for
 202 SLA20. It means that more than half of the total H_2S amount passed in the reactor was captured for
 203 SLA20. This ratio was lower for SDA20 (0.37) and equal to 0.33 for SLA10.

204

205 The 10% breakthrough was reached practically at the same time (1.8 days) for SLA10 and SDA20.
 206 This result was also observed on the Figure 2, when the curves intersect, even if the forms are
 207 different.

208 The material with the lower final mass adsorption capacity was SL (Table 2), followed by SDA20
 209 with respectively 22 and 39 mg_{H_2S}/g_{DM} , which is half the value for SLA10 ($87 mg_{H_2S}/g_{DM}$). The highest
 210 final mass adsorption capacity was obtained for SLA20 with $186 mg_{H_2S}/g_{DM}$.

211

212 As the blended AC masses within materials for each test were different, total H₂S captured can then be
 213 expressed according to AC masses to compare adsorption efficiencies of tested mixed materials. This
 214 value went from 190 to 800 mg_{H₂S}/g_{AC} respectively for SDA20 and SLA10. It is equal to 720
 215 mg_{H₂S}/g_{AC} for SLA20 . Then, it appeared that there was a created synergy between AC and SSA.

216

217 **Table 2: Synthesis of the adsorption results of mixtures**

	SL	SLA10	SLA20	SDA20
Total H₂S passed (g)	22.9 ± 1.1	30.3 ± 1.5	29.2 ± 1.5	23.6 ± 1.2
Total H₂S captured (g)	3.1 ± 0.2	10.0 ± 0.5	16.4 ± 0.8	8.7 ± 0.4
H₂S captured / H₂S passed (g/g)	0.14 ± 0.01	0.33 ± 0.02	0.56 ± 0.03	0.37 ± 0.02
10% breakthrough time (days)	-	1.8	2.7	1.8
Final adsorption capacity (mass) at the end of the test (mg_{H₂S}/g_{DM})	22 ± 1	87 ± 4	186 ± 9	39 ± 2

218

219 *3.2. Characterization of raw and used materials*

220 The materials were characterized before and after adsorption tests to better understand adsorption
 221 mechanisms taking place for each one.

222 *3.2.1. pH, water content and sulfur content*

223 SL and AC initial pH were respectively 11.4 and 10.4 (Table 3). For the SSA-based mixtures, pH went
 224 from 9.8 for SLA20 to 10.4 for SLA10. pH of SDA20 was equal to 10.4. All adsorbents were
 225 therefore basic. After adsorption tests, pH decreased for all materials. While the pH for mixtures
 226 containing SSA seemed to stabilize around 8, the pH of SDA20 fell to 2.7, becoming very acid, which
 227 must probably be limiting for H₂S chemisorption. Indeed, H₂S dissociation into HS⁻ can take place
 228 only if the pH ranges between 7.2 and 12.9. This pH sharp drop can be explained by the absence of
 229 buffer capacity for the mixture SDA20. Therefore, SSA presence is useful for stabilizing pH in a basic
 230 range, suitable for H₂S dissociation.

231

232 All materials were dried after adsorption (see Table 3). SL lost 8% of humidity. For mixed materials,
 233 humidity remained higher than 10%. It suggests that water content was not a limiting factor for H₂S

234 adsorption. The mixture SDA20 dried slightly less than the mixture with SSA, as its initial water
 235 content was lower. It can be linked with the fact that sample mass in the reactor for SDA20 was higher
 236 and consequently the water mass was also higher at the beginning of the experimental test (34 g of
 237 water for SDA20 against 23 g for SLA20).

238
 239 Sulfur content measured with CHNS analysis was also presented in the Table 3 for raw and used
 240 materials. The lowest increase of sulfur amount was remarked for SL with 2.4%S. It was consistent
 241 with H₂S mass adsorption capacity equal to 2.2%. The highest sulfur amount was measured for SLA20
 242 with 16%S for the used material and an increase of 14.4%. It was a bit lower than the mass adsorption
 243 capacity. Sulfur amounts and mass adsorption capacities were also consistent for SLA10 and SDA20.

244
 245 **Table 3: Evolution of pH, water content, sulfur content, surface area, microporous volume and**
 246 **mesoporous volume of materials before and after adsorption**

[before / after] adsorption	SL	SLA10	SLA20	SDA20
pH	11.4 ± 0.6 / 8.3 ± 0.4	10.4 ± 0.5 / 8.1 ± 0.4	9.8 ± 0.5 / 8.0 ± 0.4	10.2 ± 0.5 / 2.7 ± 0.4
Humidity (%)	19.5 ± 1.0 / 11.5 ± 0.6	20.5 ± 1.0 / 12.5 ± 0.6	20.0 ± 1.0 / 15.0 ± 0.8	15.0 ± 0.8 / 12.0 ± 0.6
Sulfur content (%)	1.4 ± 0.1 / 3.8 ± 0.2	1.6 ± 0.1 / 9.2 ± 0.5	1.7 ± 0.1 / 14.4 ± 0.7	0.5 ± 0.1 / 5.2 ± 0.3
Surface area (m².g⁻¹)	7 / 9	130 / 5	215 / 5	245 / 14
Microporous volume (cm³.g⁻¹)	0.000 / 0.000	0.048 / 0.000	0.082 / 0.000	0.095 / 0.004
Mesoporous volume (cm³.g⁻¹)	0.040 / 0.050	0.058 / 0.040	0.057 / 0.035	0.012 / 0.009

247
 248 **3.2.2. Porosity**
 249 SL had very low surface area, equal to 7 m²/g (see Table 3). The surface area of the commercial AC
 250 was 1200 m²/g. Surface areas of the mixtures were roughly equal to the weighted addition of each
 251 surface area of mixed raw materials. Indeed, surface areas of SLA20 and SLA10 were respectively
 252 equal to 215 and 130 m²/g. SDA20 had a surface area slightly higher than the mixture with SSA, with
 253 245 m²/g.

254 Regarding meso- and micropore volumes (Table 3), the total porosity of SL can be mainly represented
255 by mesopores, with a volume of 0.040 cm³/g. AC addition brought micropores: 0.082 cm³/g for
256 SLA20 and 0.048 cm³/g for SLA10. These mixtures also contained mesopores from SSA, respectively
257 0.057 and 0.058 cm³/g. The mixture with sand had less mesopores (0.012 cm³/g) which suggests that
258 AC was mainly microporous.

259 The evolution of micro and mesoporosity as well as surface area are presented in Table 3. The first
260 observation was that the porosity and the surface area of SL did not evolve after adsorption. For other
261 materials, the surface area decreased drastically. Mesoporous volume also decreased but more
262 particularly for SSA-based mixtures, as the initial mesoporous volume of SDA20 was already low.
263 Mesopores seemed therefore implied in H₂S adsorption.

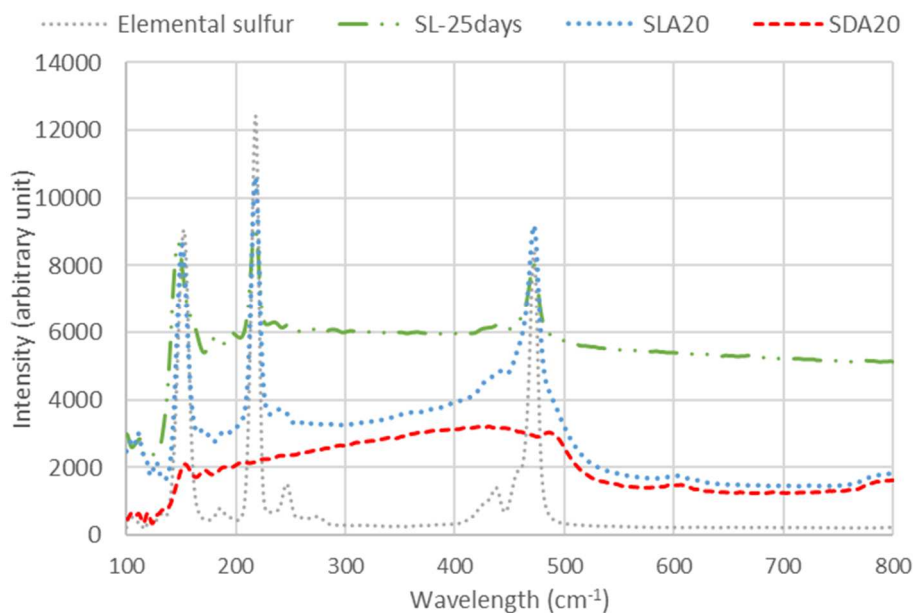
264 Concerning microporous volume, it was almost null after adsorption for all materials, no matter what
265 their initial values. H₂S adsorption was therefore related to microporous saturation. The volume loss
266 was however not proportional to the amount of H₂S adsorbed. Indeed, SDA20 lost 0.090 cm³/g of
267 microporous volume while it retained 8 g of H₂S. On the other hand, SLA20 lost 0.082 cm³/g of
268 micropores with 16.4 g of H₂S captured. Physisorption was therefore not the only explanation for H₂S
269 removal with these mixtures. Florent *et al.* also observed a steep decrease of the microporous volume
270 after adsorption for pyrolyzed mixtures composed of SS and AC (Florent *et al.*, 2019). Authors said
271 that adsorption stops when all pores are filled with sulfur.

272 **3.2.3. Raman spectroscopy**

273 Based on the literature, Raman spectroscopy can be used to validate elemental sulfur presence in
274 adsorbents (Piergrossi *et al.*, 2019). Piergrossi *et al.* observed that sulfur Raman peaks overlap with
275 the ones of AC having adsorbed sulfur.

276 As two mixtures contain SSA and AC but in different proportions (SLA10 and SLA20), only SLA20
277 was analyzed by Raman spectroscopy. Regarding SL, its adsorption capacity was only 22 mg_{H₂S}/g_{DM}
278 difficult to be quantified by analytical methods. It is the reason why another material was analyzed
279 thereafter: SL-25days. This material was the same than SL but the adsorption test lasted 25 days
280 instead of 7 days. Final mass adsorption capacity was equal to 74 mg_{H₂S}/g_{DM}.

281 Raw and used materials were analyzed by Raman spectroscopy, as well as elemental sulfur. No
282 significant peaks were observed for raw materials and it was the reason why the spectra were not
283 presented. The spectra for elemental sulfur, SL-25days, SLA20 and SDA20 after adsorption were
284 presented on the Figure 3. Three main peaks related to elemental sulfur were observed, at 152, 218 and
285 472 cm^{-1} . These peaks were also found for SL-25days and SLA20. This observation attested sulfur
286 presence in these materials. During adsorption, H_2S was therefore transformed into elemental sulfur.
287 On the other hand, no peak was observed for SDA20 even though its adsorption capacity was
288 39 $\text{mg}_{\text{H}_2\text{S}}/\text{g}_{\text{DM}}$ (non-negligible), corresponding to 34 $\text{mg}_{\text{H}_2\text{S}}/\text{cm}^3$. Preliminary analyses performed in the
289 laboratory showed that the detection limit of elementary sulfur by Raman spectroscopy was between
290 18 and 40 $\text{mg}_{\text{H}_2\text{S}}/\text{cm}^3$. It may suggest that adsorbed H_2S on SDA20 was not all transformed into S_8 by
291 chemisorption processes.



292

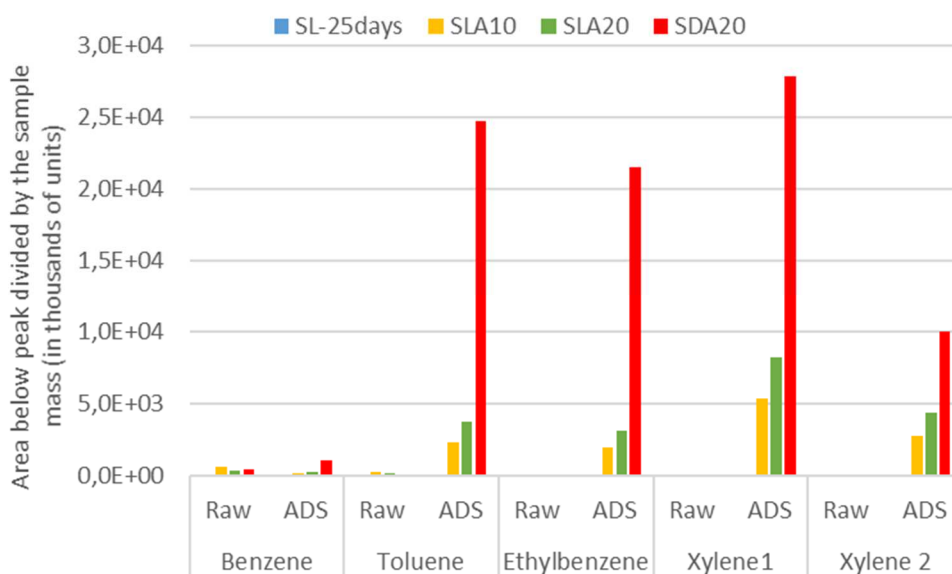
293 **Figure 3: Raman spectra of elemental sulfur, SL-25days, SLA20 and SDA20**

294

295 **3.2.4. Pyro GC-MS**

296 Pyro GC-MS analyses results cannot be quantitatively interpreted but could be qualitatively
 297 commented regarding organic compounds within different raw and used materials (Figure 4). In raw
 298 materials, few presences of volatile organic compounds were observed. Only benzene and toluene
 299 were measured in SLA20, SLA10 and SDA20. After adsorption tests, several volatile organic
 300 compounds were observed with SDA20, such as toluene, ethylbenzene or xylene (Figure 4). They
 301 were also identified in the material made from SLA20 and SLA10 but in lower amounts. These
 302 compounds could be observed by thermal decompositions of volatile organic compounds from landfill
 303 biogas. No volatile organic compounds were identified in SL-25days. While SDA20 adsorbed less
 304 sulfur than SLA20, the material retained more quantity of volatile organic compounds. This
 305 observation confirmed that AC adsorption was non-selective.

306



307

308 **Figure 4: Organic components content by Pyro GC-MS results for SL-25days, SLA10,**
 309 **SLA20 and SDA20**

310

311 **3.3. Adsorption mechanisms**

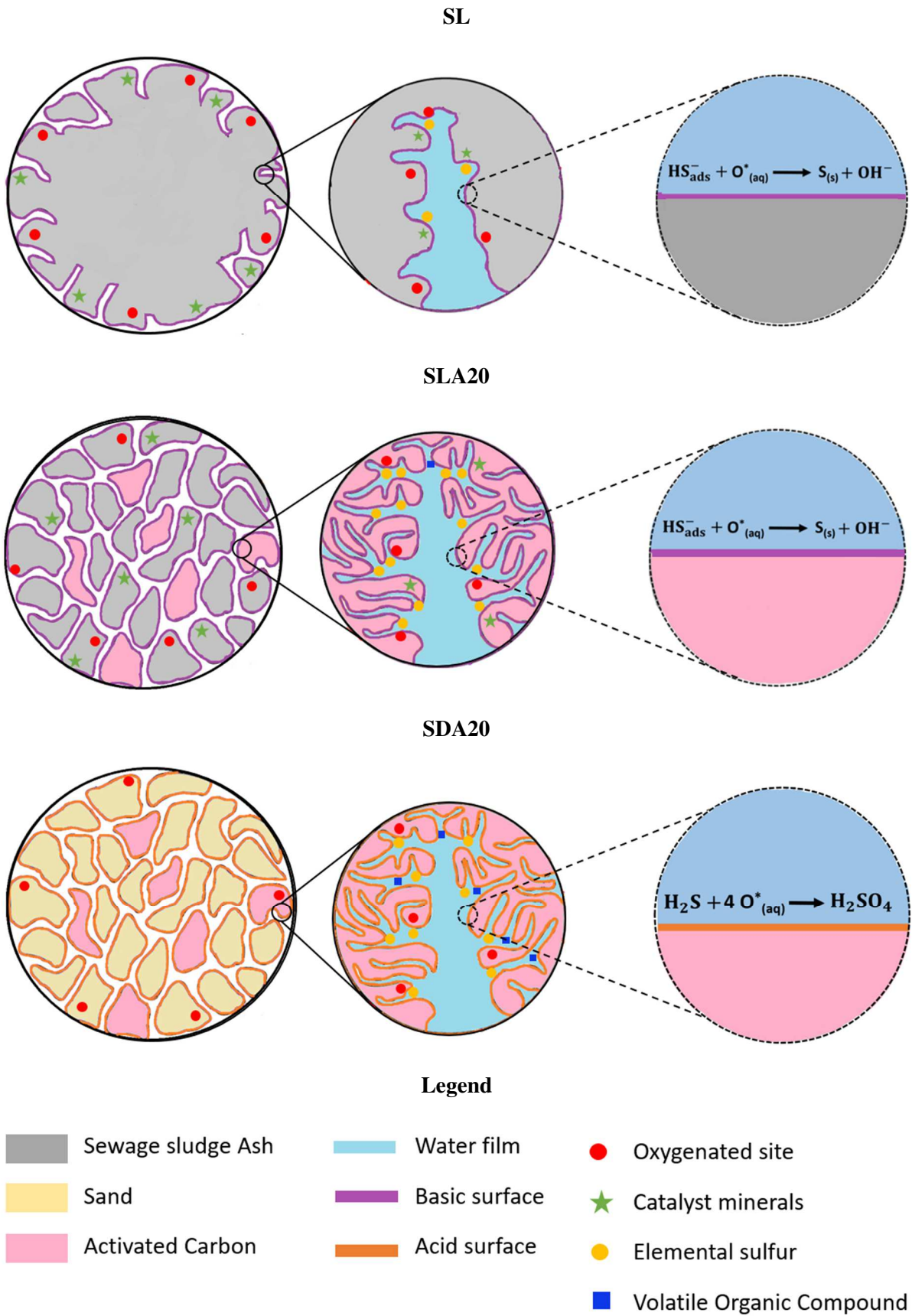
312 Materials characterization before and after H₂S adsorption provided further information about
 313 adsorption phenomena taking place within studied materials. Their adsorption mechanisms are
 314 graphically synthesized on the Figure 5.

315 In the literature concerning H₂S retention with impregnated activated carbon, it is indicated that H₂S is
316 removed via chemisorption. Indeed, if the material is basic (pH between 7.2 and 12.9), H₂S is
317 dissociated into HS⁻ and then oxidized into elemental sulfur (Bagreev and Bandosz, 2005; Xiao *et al.*,
318 2008). The larger the porosity, the more molecules can be captured (Bagreev and Bandosz, 2002).
319 Physisorption can also take place for H₂S removal but with slower kinetics.

320 SL contained oxygenated site and catalyst minerals that can promote chemisorption of H₂S (Nguyen-
321 Thanh and Bandosz, 2005) as described before. As the material was previously humidified, water
322 films surround pores. SL captured around 2% sulfur and could not retain more than 20% of the inlet
323 H₂S during the entire adsorption test. However, after one week, SL still adsorbed a little amount of
324 H₂S. SL had extremely low porosity, composed only of mesopores. This porosity did not evolve after
325 adsorption. Therefore, it seemed that the absence of micropores was the limiting factor for H₂S
326 adsorption on SL.

327 On Figure 5, SLA20 is drawn with grey grains representing SSA and pink grains representing AC. As
328 well as SL, a water film is present. The porosity is larger here with the presence of microporosity.
329 SLA20 showed the highest mass adsorption capacity, with 186 mg_{H₂S}/g_{DM}. Adsorption was efficient
330 because SLA20 had suitable characteristic. First, SLA20 had mesopores from SSA and micropores
331 brought by AC. In the literature, micropores were considered as nanoreactors for H₂S dissociation and
332 oxidation (Surra *et al.*, 2019). These micropores create reactional sites between HS⁻ and oxygen.
333 During adsorption, micropores were progressively filled, as observed previously in Table 3 with the
334 decrease of the micropores volume from 0.083 cm³/g to almost zero. The surface area of the material
335 was therefore high enough for H₂S chemisorption. Some organic compounds could nevertheless be
336 adsorbed in micropores. On the other hand, SLA20 maintained basic pH at the end of the test thanks to
337 its buffer capacity. H₂S dissociation was then not limited by pH. Besides, elemental sulfur was
338 observed in SLA20-ADS with Raman spectroscopy and Pyro GC-MS, confirming H₂S chemisorption.
339 By Sioukri *et al.*, synergy between AC and SSA was reported thanks to the combined presence of
340 small pores (around 1 nm) and catalytic centers (Sioukri *et al.*, 2005). It would favor as-formed sulfur
341 retention, filling progressively all the porous volume. However, the porous network must be
342 sufficiently interconnected to make the small pores easily available.

343 CHNS analysis indicated that SDA20 contains 5.2% of sulfur after adsorption test. According to
344 characterization results, it seemed that SDA20 adsorption takes place in several steps. At the
345 beginning of the test, SDA20 was wet (15 % w/w of humidity) and the pH was basic (10.4). With
346 these conditions, H₂S dissociated into HS⁻ then oxidized into elemental sulfur thanks to oxygen
347 presence within biogas. However, SDA20 had no buffer capacity so could not maintain basic pH until
348 the end of adsorption tests. pH decreased quickly due to the contact with acid gas (H₂S and CO₂), yet
349 when pH is below seven, H₂S can be only physisorbed. Moreover, the significant presence of
350 elemental sulfur was not observed with Raman spectroscopy within SDA20, suggesting that H₂S may
351 not be mainly adsorbed under elemental sulfur form within this material. Indeed, a pH of 2.7 was
352 certainly due to the acid sulfuric formation. Non-selective physisorption can also take place
353 simultaneously. Landfill biogas organic compounds were identified in significant amounts by pyro
354 GC-MS within SDA20. These compounds were represented with a blue square on the drawing on the
355 Figure 5. Microporosity was the main driver of this physisorption. Indeed, at the end of adsorption
356 tests, SDA20 micropore volume was almost null while it was equal to 0.095 cm³/g for the raw sample.
357



358

Figure 5: Schematic mechanisms with each material

359

360 **4. Conclusions**

361 The adsorption tests during this study highlighted interesting potential of SSA when it was mixed with
362 AC for H₂S removal. Indeed, removal capacities of the material are significantly improved, even if
363 only 10% of AC was added. For a same amount of H₂S passed, SSA adsorbs 22 mg_{H₂S}/g_{DM} while
364 SLA10 retains two times more H₂S and SLA20 five times more. Besides, these mixtures capture the
365 whole H₂S entering during the first day of the adsorption test which was not the case for SSA. It is an
366 important feature for using these materials as H₂S adsorbents at industrial scale

367 Comparing sand/AC mixture test with SSA/AC mixtures test showed that good H₂S adsorption
368 capacity for mixture SSA/AC was due to a synergy of both materials, having complementary
369 physicochemical characteristics and not only an improvement of adsorption capacity. SSA can then be
370 seen as a “low cost” impregnated material to improve the AC adsorption capacity. More than that, in
371 order to save resources and participate to circular economy, mixing SSA with a porous material is a
372 promising way to valorize SSA and to reduce energy production costs from biogas.

373

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