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► To cite this version:

Valentine Gasquet, Boram Kim, Anne Bonhomme, Hassen Benbelkacem. Sewage sludge ash-derived materials for H2S removal from a landfill biogas. Waste Management, 2021, 136, pp.230-237. 10.1016/j.wasman.2021.10.023 . hal-04185197

HAL Id: hal-04185197 https://hal.science/hal-04185197

Submitted on 5 Jan 2024

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Version of Record: https://www.sciencedirect.com/science/article/pii/S0956053X21005638 Manuscript_b47ba2cb3da205b84dfc757e09320a2d

¹ Sewage Sludge Ash-derived materials for H₂S

² removal from a landfill biogas

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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 H_2S 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 H_2S dissociation into HS^- then its chemisorption. On the other hand, 19 with the microporosity of AC, the contact surface between H_2S and oxygen was sufficiently large for 20 chemisorption kinetics. It also appeared that the mixture with sand and AC adorbs 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

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26 1. Introduction

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

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A European directive (200/60/EC) adopted on October 23rd 2000 defined sludge not as a waste 34 35 material but as a product of sewage treatment (European Parliament, Directive 2000/60/EC). The conurbations must monitor and report sewage treatments and sludge disposal (Kacprzak et al., 2017). 36 The European Parliament and Council Directive 2008/98/EC of November 19th 2008 states that a 37 priority in SS management is its preparation in order to reuse, recycle or recover it in another form 38 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 for SS management to reduce its volume. Indeed, in European Union, approximatively 10 Mt dry mass 41 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).

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On the other hand, another current issue is energy production and the limitation of CO_2 emissions. Renewable energy development is therefore necessary. Biogas is a renewable gas obtained by the anaerobic digestion of organic waste, such as SS. Biogas' advantages are its non-intermittence, the possibility to produce it locally (and consequently less transport) and its different uses. Indeed, biogas can be valorized for heat and power generation with a CHP unit, as a fuel for vehicles (compressed or liquefied) and injected into the gas grid, for domestic or industrial use.

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

SS has been used as precursor for adsorbents production, after a pyrolysis (Bagreev et al., 2001; Ros et 64 al., 2006; Gutiérrez Ortiz et al., 2014). This thermal treatment develops the material porosity, with 65 surface area going from 12 to 248 m²/g (Wallas et al., 2014; Possa et al., 2018). The pyrolyzed sludge 66 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., 2017), with HCl (Possa et al., 2018) or activated with CO₂ (Wallas et al., 2014). Adsorption capacities 69 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 H_2S 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

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

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

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The objective of this work is to estimate the potential of SSA itself and SSA blended with AC as adsorbent for H_2S removal from a real landfill biogas and to understand related adsorption mechanisms.

91

92 2. Materials and methods

93 2.1. Materials

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

Primary test showed that the adsorption efficiency increases with humidity (result not shown here).
For adsorption experiment, SSA was humidified at 20%m. Distilled water was slowly added to the
raw material with a continuous stirring. Mixtures were realized by mixing SSA or sand with AC in
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

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

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117 2.2. Biogas adsorption tests

The experimental set-up for biogas adsorption tests was described previously (Gasquet et al., 2020) 118 and the diagram is presented on the Figure 1. To summarize, experiments were realized on a landfill, 119 120 using a real biogas. Consequently, the inlet biogas composition did not stay constant for all the tests. 121 The mean H_2S concentration ranged between 1415 to 1715 ppm_y, as observed in Table 1. Indeed, depending on the grid management, some air can be introduced in the biogas and diluted it. Moreover, 122 123 for the same reason, H₂S concentration can reach 5000 ppm_v during a short period. These variations may have an influence on the amount of H_2S captured and it is therefore important to consider it. The 124 125 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 experiments (251 cm³), with a fixed height in the reactor equal to 20 cm. This is the reason why the 128 mass of dry sample was different for each case, with different densities, from 0.9 for SL to 2.65 for 129 SDA20 (see Table 1). Hence, the AC mass was different for each test, with respectively 11.4, 21.9 and 130 131 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 composition was analyzed with an infrared laser spectrometer called ProCeas. Biogas bubbles in a vial 133 containing water before the reactor to humidify it. 134





Figure 1 : Lab-scale adsorption pilot

137

In order to compare the materials, some parameters are calculated. First, H_2S_{passed} and $H_2S_{captured}$ are calculated as presented in equations (1) and (2), with $[H_2S]_{inlet}$ and $[H_2S]_{outlet}$ respectively the inlet and outlet H_2S concentration in g/m³. \dot{V} represents the gas flow in m³/min. Mass adsorption capacity is obtained by dividing the H_2S amount removed by the dry mass of the adsorbent. The H_2S amount captured at which point the ratio $[H_2S]_{outlet}/[H_2S]_{inlet}$ is equal to 0.1 (10%) is also compared for the materials.

$$H_2 S_{passed} = \int_0^t [H_2 S]_{inlet}(t) \times \dot{V}(t) dt$$
(1)

$$H_2 S_{captured} = \int_0^t ([H_2 S]_{inlet}(t) - [H_2 S]_{outlet}(t)) \times \dot{V}(t) dt$$
(2)

144

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

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

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2.3. Materials characterization

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

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

159

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

165

Raman spectroscopy was realized at room temperature under air with a Kaiser RXN1 and a Charged-Coupled Device of the same brand. Spectra were obtained with an excitation laser working at a wavelength of 785 nm. The acquisition spectral region goes from 100 to 3420 cm⁻¹ with a resolution of 4 cm⁻¹. Pyrolysis with Gas Chromatography-Mass Spectroscopy (Pyro GC-MS) consists of an analysis of the gaseous components produced during a flash pyrolysis, at 550°C. 1 to 2 mg of sample was introduced in the pyrolyzer (EGA/Py-3030D model from Frontier Lab) at the desired temperature under inert gas (He). The pyrolysis gas was drawn to the chromatography column (HP-5ms). After this column, the mass spectrometer (simple quadrupole model 5977B from Agilent) detects the components depending on the ratio mass to charge (m/z).

175

176 **3. Results**

177 3.1. Comparison of H_2S removal efficiencies

On the Figure 2, the evolution of the ratio [H₂S]_{outlet} over [H₂S]_{inlet} also called C/C₀ is observed as a
function of the time for the SL, SLA10, SLA20 and SDA20.

180

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

187

188 The three materials containing AC could remove all H₂S during the first day. The breakthrough was first observed for SLA10 after one day, and then for SDA20 after 1.7 days. Finally the last 189 breakthrough was observed for SLA20 (2.7 days). The curve slope was not either the same, with a 190 steeper slope for SDA20. This material reached faster its total saturation. A peak was observed for 191 192 SLA10 at 2.8 days. It can be explained by a quick rise of H_2S inlet concentration (5000 ppm_y) due to 193 the landfill grid management. At this point, inlet H₂S amount was too high for materials to adsorb the 194 same H_2S fraction than the one adsorbed when H_2S inlet concentration was 1500 ppm_y. Finally, after 6 195 days, all materials removed less than 25% of the inlet H₂S.







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

199

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

204

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

The material with the lower final mass adsorption capacity was SL (Table 2), followed by SDA20 with respectively 22 and 39 mg_{H2S}/g_{DM} , which is half the value for SLA10 (87 mg_{H2S}/g_{DM}). The highest final mass adsorption capacity was obtained for SLA20 with 186 mg_{H2S}/g_{DM} .

- As the blended AC masses within materials for each test were different, total H₂S captured can then be expressed according to AC masses to compare adsorption efficiencies of tested mixed materials. This value went from 190 to 800 mg_{H2S}/g_{AC} respectively for SDA20 and SLA10. It is equal to 720 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 H ₂ S passed (g)	22.9 ± 1.1	30.3 ± 1.5	29.2 ± 1.5	23.6 ± 1.2
Total H ₂ S captured (g)	3.1 ± 0.2	10.0 ± 0.5	16.4 ± 0.8	8.7 ± 0.4
H ₂ S captured / H ₂ S 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

SL and AC initial pH were respectively 11.4 and 10.4 (Table 3). For the SSA-based mixtures, pH went 223 from 9.8 for SLA20 to 10.4 for SLA10. pH of SDA20 was equal to 10.4. All adsorbents were 224 therefore basic. After adsorption tests, pH decreased for all materials. While the pH for mixtures 225 226 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 H_2S chemisorption. Indeed, H_2S dissociation into HS^- can take place only if the pH ranges between 7.2 and 12.9. This pH sharp drop can be explained by the absence of 228 buffer capacity for the mixture SDA20. Therefore, SSA presence is useful for stabilizing pH in a basic 229 230 range, suitable for H₂S dissociation.

231

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

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

238

Sulfur content measured with CHNS analysis was also presented in the Table 3 for raw and used materials. The lowest increase of sulfur amount was remarked for SL with 2.4%S. It was consistent with H₂S mass adsorption capacity equal to 2.2%. The highest sulfur amount was measured for SLA20 with 16%S for the used material and an increase of 14.4%. It was a bit lower than the mass adsorption 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	f materials	before and	l after	adsor	ptior
	mesoporous	, oranie or	. Interver terio	Nerore and	A COLUCI	a cabor	

[before / after] adsorption	SL	SLA10	SLA20	SDA20
рН	$11.4 \pm 0.6 / 8.3 \pm 0.4$	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	$20.5 \pm 1.0 /$ 12.5 ± 0.6	$20.0 \pm 1.0 /$ 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 (m ² .g ⁻¹)	7/9	130/5	215/5	245 / 14
Microporous volume (cm ³ .g ⁻¹)	0.000 / 0.000	0.048 / 0.000	0.082 / 0.000	0.095 / 0.004
Mesoporous volume (cm ³ .g ⁻¹)	0.040 / 0.050	0.058 / 0.040	0.057 / 0.035	0.012 / 0.009

247

248 *3.2.2.Porosity*

SL had very low surface area, equal to 7 m²/g (see Table 3). The surface area of the commercial AC was 1200 m²/g. Surface areas of the mixtures were roughly equal to the weighted addition of each surface area of mixed raw materials. Indeed, surface areas of SLA20 and SLA10 were respectively equal to 215 and 130 m²/g. SDA20 had a surface area slightly higher than the mixture with SSA, with 245 m²/g. Regarding meso- and micropore volumes (Table 3), the total porosity of SL can be mainly represented by mesopores, with a volume of 0.040 cm³/g. AC addition brought micropores: 0.082 cm³/g for SLA20 and 0.048 cm³/g for SLA10. These mixtures also contained mesopores from SSA, respectively 0.057 and 0.058 cm³/g. The mixture with sand had less mesopores (0.012 cm³/g) which suggests that AC was mainly microporous.

The evolution of micro and mesoporosity as well as surface area are presented in Table 3. The first observation was that the porosity and the surface area of SL did not evolve after adsorption. For other materials, the surface area decreased drastically. Mesoporous volume also decreased but more particularly for SSA-based mixtures, as the initial mesoporous volume of SDA20 was already low. Mesopores seemed therefore implied in H_2S adsorption.

Concerning microporous volume, it was almost null after adsorption for all materials, no matter what 264 265 their initial values. H₂S adsorption was therefore related to microporous saturation. The volume loss was however not proportional to the amount of H₂S adsorbed. Indeed, SDA20 lost 0.090 cm³/g of 266 microporous volume while it retained 8 g of H₂S. On the other hand, SLA20 lost 0.082 cm³/g of 267 268 micropores with 16.4 g of H₂S captured. Physisorption was therefore not the only explanation for H₂S removal with these mixtures. Florent et al. also observed a steep decrease of the microporous volume 269 270 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

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

As two mixtures contain SSA and AC but in different proportions (SLA10 and SLA20), only SLA20 was analyzed by Raman spectroscopy. Regarding SL, its adsorption capacity was only 22 mg_{H2S}/g_{DM} difficult to be quantified by analytical methods. It is the reason why another material was analyzed thereafter: SL-25days. This material was the same than SL but the adsorption test lasted 25 days instead of 7 days. Final mass adsorption capacity was equal to 74 mg_{H2S}/g_{DM}. Raw and used materials were analyzed by Raman spectroscopy, as well as elemental sulfur. No significant peaks were observed for raw materials and it was the reason why the spectra were not presented. The spectra for elemental sulfur, SL-25days, SLA20 and SDA20 after adsorption were presented on the Figure 3. Three main peaks related to elemental sulfur were observed, at 152, 218 and 472 cm⁻¹. These peaks were also found for SL-25days and SLA20. This observation attested sulfur presence in these materials. During adsorption, H_2S was therefore transformed into elemental sulfur.

On the other hand, no peak was observed for SDA20 even though its adsorption capacity was 39 mg_{H2S}/g_{DM} (non-negligible), corresponding to 34 mg_{H2S}/cm³. Preliminary analyses performed in the laboratory showed that the detection limit of elementary sulfur by Raman spectroscopy was between 18 and 40 mg_{H2S}/cm³. It may suggest that adsorbed H₂S on SDA20 was not all transformed into S₈ by chemisorption processes.





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

295 *3.2.4.Pyro GC-MS*

Pyro GC-MS analyses results cannot be quantitatively interpreted but could be qualitatively 296 297 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 sulfur than SLA20, the material retained more quantity of volatile organic compounds. This 304 305 observation confirmed that AC adsorption was non-selective.

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307



Figure 4: Organic components content by Pyro GC-MS results for SL-25days, SLA10,

SLA20 and SDA20

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- 310

311 3.3. Adsorption mechanisms

312 Materials characterization before and after H_2S adsorption provided further information about 313 adsorption phenomena taking place within studied materials. Their adsorption mechanisms are 314 graphically synthetized on the Figure 5. In the literature concerning H_2S retention with impregnated activated carbon, it is indicated that H_2S is removed via chemisorption. Indeed, if the material is basic (pH between 7.2 and 12.9), H_2S is dissociated into HS^- and then oxidized into elemental sulfur (Bagreev and Bandosz, 2005; Xiao *et al.*, 2008). The larger the porosity, the more molecules can be captured (Bagreev and Bandosz, 2002). Physisorption can also take place for H_2S removal but with slower kinetics.

SL contained oxygenated site and catalyst minerals that can promote chemisorption of H_2S (Nguyen-Thanh and Bandosz, 2005) as described before. As the material was previously humidified, water films surround pores. SL captured around 2% sulfur and could not retain more than 20% of the inlet H_2S during the entire adsorption test. However, after one week, SL still adsorbed a little amount of H_2S . SL had extremely low porosity, composed only of mesopores. This porosity did not evolve after adsorption. Therefore, it seemed that the absence of micropores was the limiting factor for H_2S adsorption on SL.

On Figure 5, SLA20 is drawn with grey grains representing SSA and pink grains representing AC. As
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 because SLA20 had suitable characteristic. First, SLA20 had mesopores from SSA and micropores 330 brought by AC. In the literature, micropores were considered as nanoreactors for H₂S dissociation and 331 332 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 decrease of the micropores volume from 0.083 cm³/g to almost zero. The surface area of the material 334 335 was therefore high enough for H_2S 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 small pores (around 1 nm) and catalytic centers (Sioukri et al., 2005). It would favor as-formed sulfur 340 retention, filling progressively all the porous volume. However, the porous network must be 341 sufficiently interconnected to make the small pores easily available. 342

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 the end of adsorption tests. pH decreased quickly due to the contact with acid gas (H₂S and CO₂), yet 348 349 when pH is below seven, H₂S can be only physisorbed. Moreover, the significant presence of elemental sulfur was not observed with Raman spectroscopy within SDA20, suggesting that H₂S may 350 not be mainly adsorbed under elemental sulfur form within this material. Indeed, a pH of 2.7 was 351 certainly due to the acid sulfuric formation. Non-selective physisorption can also take place 352 353 simultaneously. Landfill biogas organic compounds were identified in significant amounts by pyro GC-MS within SDA20. These compounds were represented with a blue square on the drawing on the 354 Figure 5. Microporosity was the main driver of this physisorption. Indeed, at the end of adsorption 355 tests, SDA20 micropore volume was almost null while it was equal to 0.095 cm³/g for the raw sample. 356



SLA20



Figure 5: Schematic mechanisms with each material

360 4. Conclusions

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

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

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374 Acknowledgements

375 The authors are grateful for the fnancial support provided by the Agence de l'Eau Rhône Méditerranée

376 Corse (VALBIFIL project). They also thank Hervé Perier-Camby and Richard Poncet (DEEP

377 laboratory– INSA Lyon, France) for their technical support. This work was performed within the

- 378 framework of the EUR H2O'Lyon (ANR-17-EURE-0018) of Université de Lyon (UdL), within the
- 379 program "Investissements d'Avenir" operated by the French National Research Agency (ANR).

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