Adsorption of hydrogen sulphide on activated carbon materials derived from the solid fibrous digestate

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Introduction

The goal of this work is to develop a sustainable value chain of carbonaceous adsorbents that can be produced from the solid fibrous digestate (SFD) of biogas plants and further applied in integrated desulphurisation-upgrading (CO_2/CH_4 separation) processes of biogas to yield high purity biomethane.

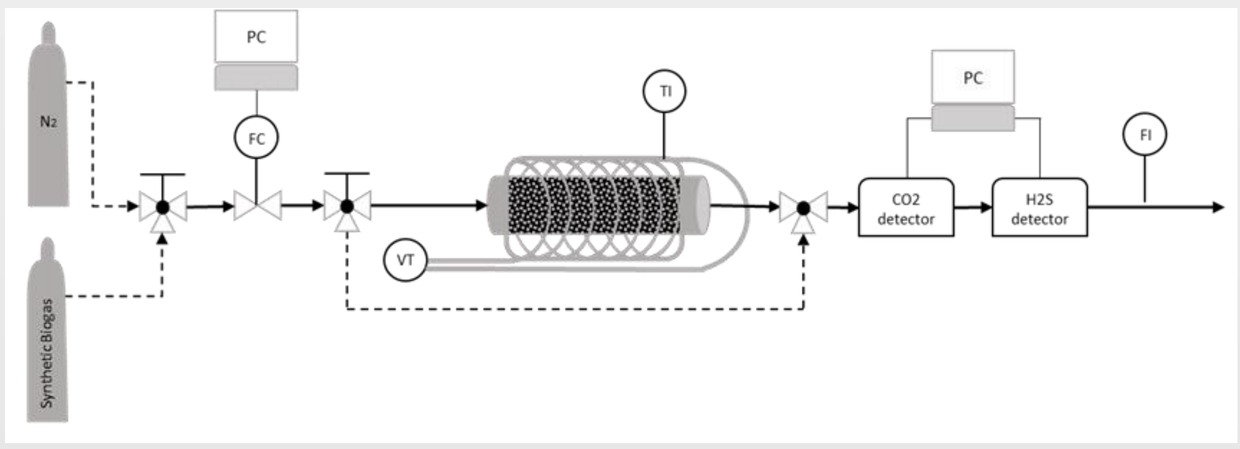
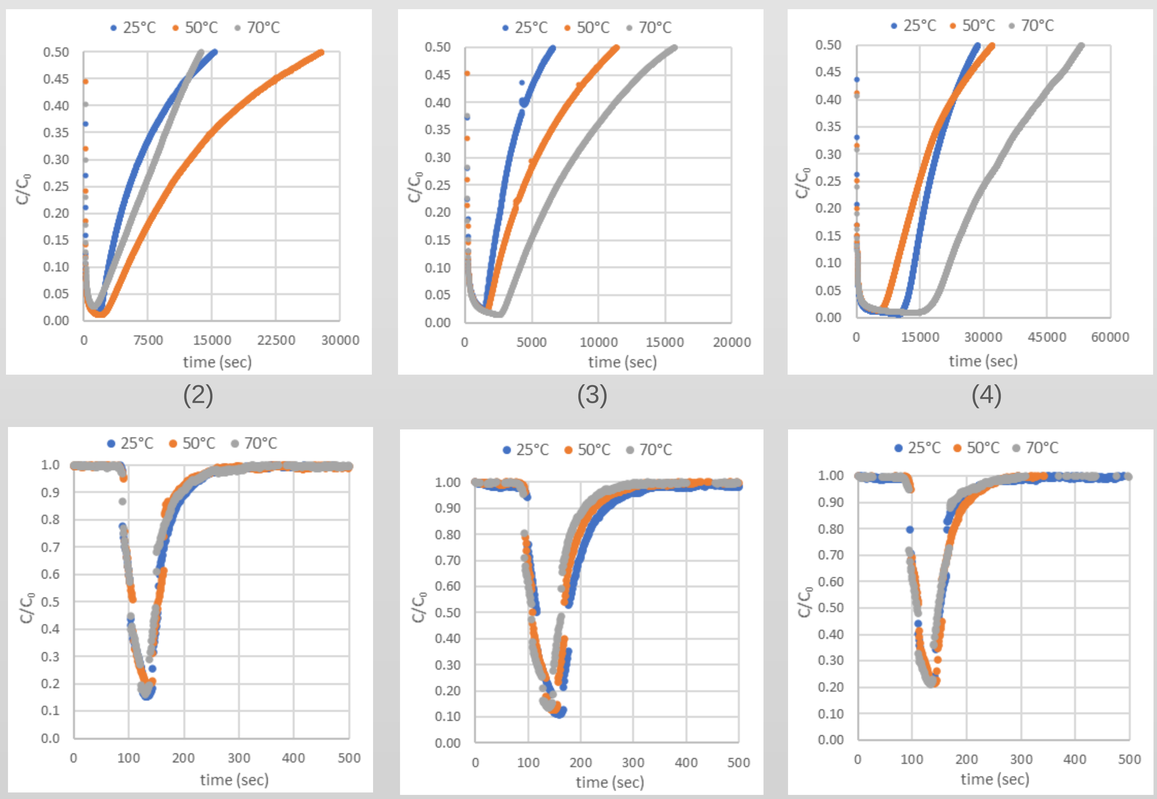


Figure 1: Adsorption Reactor System; FC: Flow Controller, VT: Variac Transformer, TI: Temperature Indicator, FI: Flow Indicator.

On this purpose, physical and chemical activation of the SFD derived biochar was optimised to afford micro-mesoporous activated carbons (ACs) of high BET surface area (590-2300 m^2g^{-1}) and enhanced pore volume (0.57-1.0 cm^3g^{-1}). Gas breakthrough experiments of the obtained ACs were performed on a fixed bed column, using real biogas mixture as feedstock. The adsorption experimental system consists of 3 parts; the inlet gas part, the adsorption reactor and a gas detection system. There are 2 bottles with gases, one with Nitrogen and one with the synthetic biogas (57%CH_4, 42%CO_2, 0,5%O_2 and 500ppm H_2S). The inlet gas flow rates are controlled by a mass flow controller and a valve to perform the flow task of choosing whether Nitrogen or Biogas mixture will be inserted in the reactor. The adsorption reactor is a horizontal stainless steel tubular fixed bed 7.9cm long and of 4.8mm inner diameter.

Results & Discussion



Figures 2-7: Adsorption curves of H_2S on activated carbons with H_2O (2), with KOH (3) and with CO_2 (4); adsorption curves of CO_2 on activated carbons with H_2O (5), with KOH (6) and with CO_2 (7)

Performing breakthrough experiments at three temperatures close to ambient it was possible to calculate the steric heat of sorption and define the optimum conditions for enhanced H_2S/CO_2 separation. It was also concluded that the H_2S adsorption capacity is significantly affected by restriction to gas diffusion. Hence, the best performance was obtained at 70°C and the maximum observed in the H_2S adsorption capacity vs the temperature is attributed to the counterbalance between adsorption and diffusion into micropores.

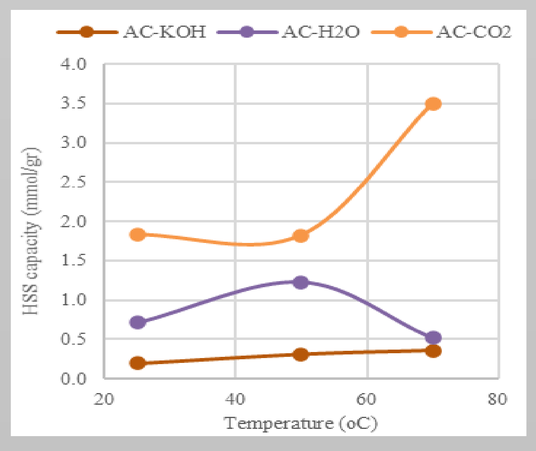


Figure 8: H_2S capacity of the activated carbons

Selectivity of H_2S over CO_2 is high for all the activated carbon samples (from 132 to 22,859) with the highest value on the activated carbon with CO_2 when adsorption takes place at 70°C while for the activated carbon with steam the highest value of selectivity is noted at adsorption temperature 50°C (2,719). The lowest selectivity of H_2S is noted when adsorption happens on the chemically functionalized carbon with KOH at 25°C.

The SFD (solid fraction of digestate) is obtained from the whole digestate of the anaerobic digester of a biogas plant, after filtration in a filter press; followed by drying. The total yield of the SFD is about 25%. In order to remove the inorganic compounds from the surface of the SFD precursor materials oxidation by HNO_3 1% solution performed and oxidized (washed) materials, SFD-W, were obtained. The carbonization was carried out in a bench scale fixed bed reactor investigating the temperature parameter (600-800°C) along with the residence time of the pyrolysis (30-120mins).

Biochar materials derived from the carbonization of the untreated SFD (BC-SFD) had higher ash content (more than 33.60%) while the pretreated BC-SFD-W materials had less than half ash content (up to 18.10%); this indicates the removal of part of the inorganic compounds (~72%) on the surface of the precursor material with the HNO_3 pretreatment and allowing the carbonization process to expand the carbon matrix. Moreover, biochar materials derived from the carbonization of the untreated SFD (BC-SFD) had very low BET specific surface area (<50m^2/g) compared to biochar samples obtained from the pretreated with HNO_3 1% solution, SFD-W (BC-SFD-W), (up to 363m^2/g).

Biochar obtained by SFD-W were functionalized into activated carbon using physical activation with H_2O and CO_2, and chemical activation with KOH, producing micro-mesoporous carbonaceous materials, with BET surface areas between 585 and 2299 m^2/g and pore volumes between 0.569 and 1.010 cm^3/g

Table 1: H_2S adsorption capacity, molar mass and mass of H_2S adsorbed per AC mass, on the activated carbon materials in various adsorption temperatures.

Activated carbon	Adsorption temperature (°C)	H_2S capacity (mmol[H_2S]/g)			H_2S capacity (g[H_2S]/g) at Reference time C/C_0=0.5 [1]
		Breakthrough time (C/C_0=0.05) [1]	**Reference time C/C_0=0.5 [1]**	Exhaustion time (C/C_0=0.95) [2]	
AC-H_2O	25	0.10	0.71	2.13	20.93
	50	0.09	1.22	3.26	35.94
	70	0.04	0.51	1.54	15.02
AC-KOH	25	0.05	0.19	0.88	5.66
	50	0.05	0.31	1.42	9.03
	70	0.07	0.36	0.79	10.47
AC-CO_2	25	0.75	1.83	4.70	53.62
	50	0.36	1.82	4.63	53.44
	70	0.86	3.50	7.51	20.93

Table 2. CO_2 adsorption capacity, molar mass and mass of CO_2 adsorbed per AC mass, on the activated carbon materials in various adsorption temperatures.

Activated carbon	Adsorption temperature (°C)	CO_2 capacity (mmol[CO_2]/g)			CO_2 capacity (g[CO_2]/g) at Reference time C/C_0=0.5 [1]
		Breakthrough time (C/C_0=0.05) [1]	Reference time C/C_0=0.5 [1]	**Exhaustion time (C/C_0=0.95) [1]**	
AC-H_2O	25	0.08	0.19	0.30	6.82
	50	0.00	0.15	0.36	8.18
	70	0.11	0.20	0.38	8.63
AC-KOH	25	0.21	0.62	1.17	26.58
	50	0.13	0.49	0.86	19.54
	70	0.04	0.37	0.54	12.27
AC-CO_2	25	0.07	0.17	0.38	8.63
	50	0.06	0.10	0.10	2.27
	70	0.05	0.11	0.12	2.73

Conclusions

Gas breakthrough experiments from fixed bed columns of the obtained ACs, using real biogas mixture as feedstock, unveiled that the physical and chemical activation conclude to different types of ACs which are sufficient for biogas upgrade and biogas desulphurisation respectively.

- The higher the specific surface area the more H_2S is adsorbed from the AC while the higher the BET specific surface area the more CO_2 is adsorbed.
- The H_2S adsorption capacity is significantly affected by restriction to gas diffusion.
- AC-H_2O has lower BET surface area than AC-CO_2 and adsorbs more H_2S at 50°C and less at 70°C while AC-CO_2 adsorbs the most H_2S at 70°C.

The highest selectivity of hydrogen sulfide adsorption over CO_2 is achieved for 70°C, followed by 50°C adsorption temperature on the activated carbon physically functionalized with CO_2 .

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