PERFORMANCE AND CHARACTERIZATION OF TWO ACTIVATED CARBONS FOR BIOGAS TREATMENT APPLICATIONS

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INTRODUCTION

CONTEXT

Why biogas production and end-use needs to be addressed?

- The fossil-based energy is depleting
- The green hose gases emissions contribute to climate change
- The demand for energy is constantly increasing
- The cost of energy is increasing
- The requirements to reduce the energy consumption in WWTP

Emerging technologies: Promising technically, environmentally

- **Raw Sewage Biogas** → **Cleaning (H_2S, water,...)** → **Clean Sewage Biogas**
- **Reforming ($CH_4 \rightarrow H_2$) + use in low Tº fuel cells** / **Direct use in high Tº fuel cells** / **Classical cogeneration** → **Combined Heat and Power**

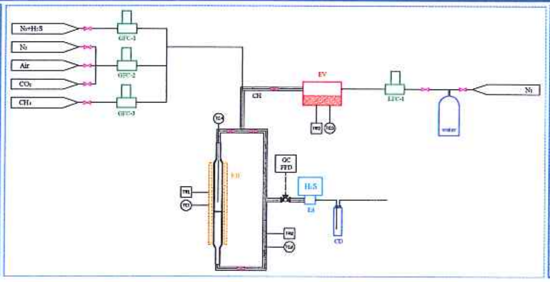
OBJECTIVES

The aim of the project is the study of sulfur removal through adsorption systems, investigating the behavior and adsorption capacity of some commercial adsorbent materials. In particular, two impregnated activated carbons, AC Airpel Ultra DS supplied by Desotec and AC RGM1 supplied by Norit, have been tested using different matrices, including biogas ones, in dry and wet conditions and also in presence of small percentages of oxygen in the gas carrier. Moreover, the characterization of the adsorbent materials before and after their use is done through nitrogen adsorption-desorption measurements, to verify modifications in terms of specific surface area and/or micropore volume.

TEST BENCH DESCRIPTION AND METHODOLOGY

The inlet gas mixture was supplied by gas mass flow meter controllers, realizing a wide range of H2S concentrations and different combinations of carrier gases (N_2/CO_2/CH_4/Air).

The tests with different percentages of humidity were performed adding to the gas mixture the desired amount of water vapor, using a liquid flow meter controller and an evaporator. After the injection of water, the temperature of the pipelines was controlled using cable heaters, to avoid the condensation of water.



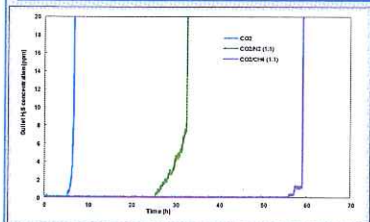
The H_2S adsorption capacity (Cads in mg/g) is calculated from the breakthrough curves using the following equation:

$$C_{ads} = \frac{Q_{tot}\cdot MW\cdot[C_{in}\cdot t_1 - (t_1 - t_0)\cdot 0.5]}{V_m\cdot m\cdot 10^3}$$

Q_{tot} = total gas flow rate (Nl/h);
MW = molecular weight (H_2S = 34 g/mol);
C_{in} = inlet H_2S concentration (ppmv);
t_1 = breakthrough time when the outlet H_2S concentration is 1 ppmv (h);
t_0 = breakthrough time at the last detection of 0 ppmv (h);
V_m = molar volume (24,414 Nl/mol);
m = mass of adsorbent material (g).

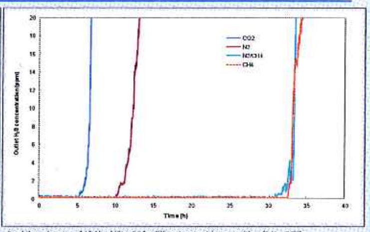
RESULTS AND DISCUSSION

GAS MATRIX EFFECT



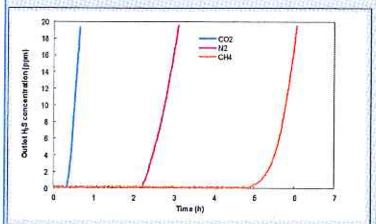
Influence of CO_2 on H_2S adsorption of AC Airpel Ultra DS (R.H. 90%, GHSV 10000 h^{-1}, inlet H_2S 100 ppmv).

Gas matrix	t_0 (h)	t_1 (h)	C_{ads} (mg/g)
CO_2	5.35	5.85	19.29
CO_2/N_2 (1:1)	25.42	26.48	87.36
CO_2/CH_4 (1:1)	55.80	57.20	188.72



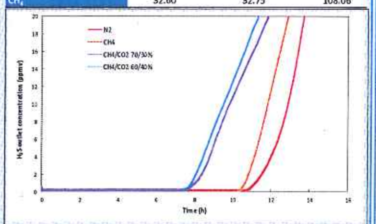
Breakthrough curves of AC Airpel Ultra DS for different gas matrix compositions (R.H. = 90%).

Gas matrix	t_0 (h)	t_1 (h)	C_{ads} (mg/g)
CO_2	5.35	5.85	19.29
N_2	10.15	10.57	34.87
N_2/CH_4 (1:1)	31.27	31.92	105.32
CH_4	32.60	32.75	108.06



Breakthrough curves of AC Airpel Ultra DS for different gas matrix compositions (dry conditions).

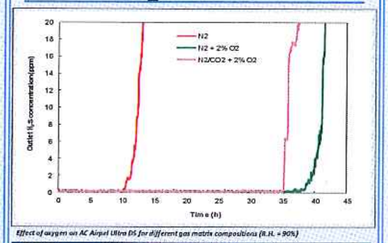
Gas matrix	t_0 (h)	t_1 (h)	C_{ads} (mg/g)
CO_2	0.33	0.37	1.22
N_2	2.20	2.30	7.59
CH_4	4.88	5.17	17.06



Breakthrough curves of AC RGM1 for different gas matrix compositions (dry conditions).

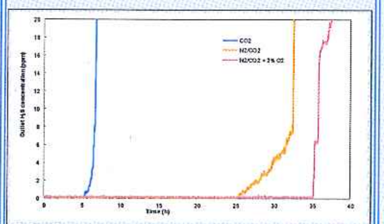
Gas matrix	t_0 (h)	t_1 (h)	C_{ads} (mg/g)
N_2	10.89	11.14	34.69
CH_4	10.31	10.64	33.11
CH_4/CO_2 (70/30%)	7.73	7.99	24.88
CH4/CO2 (60/40%)	7.51	7.83	24.37

O_2 EFFECT



Effect of oxygen on AC Airpel Ultra DS for different gas matrix compositions (R.H. = 90%)

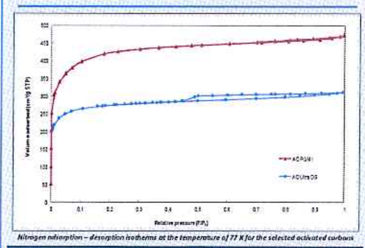
Gas Matrix	O_2 concentration (%)	t_0 (h)	t_1 (h)	C_{ads} (mg/g)
N_2	0	10.15	10.57	34.87
N_2	2	37.70	38.68	127.62
N_2/CO_2	2	35.13	35.18	116.08



Effect of oxygen and CO_2 on AC Airpel Ultra DS (R.H. = 90%)

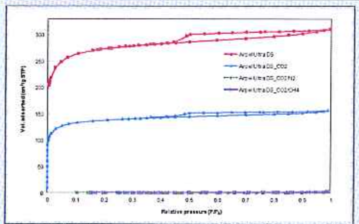
Gas matrix	t_0 (h)	t_1 (h)	C_{ads} (mg/g)
CO_2	5.35	5.85	19.29
CO_2/N_2 (1:1)	25.42	26.48	87.36
CO_2/N_2 (1:1) + 2% O_2	35.13	35.18	116.08

CHARACTERIZATION



Nitrogen adsorption – desorption isotherms at the temperature of 77 K for the selected activated carbons

Sample	$A_{B.E.T}$ (m^2/g)	V_μ (cm^3/g)
AC Norit RGM1	1599	0.66
AC Desotec Airpel Ultra DS	1042	0.42



Nitrogen adsorption – desorption isotherms at the temperature of 77 K for the virgin and spent samples of AC Desotec Airpel Ultra DS after the runs performed with R.H. 90% varying gas matrix composition

Sample	BET surface area (m^2/g)	Micropore volume (cm^3/g)
AC Ultra DS	1042	0.42
AC Ultra DS_CO_2	527	0.18
AC Ultra DS_CO_2/N_2 (1:1)	1.42	0
AC Ultra DS_CO_2/CH_4 (1:1)	1.38	0

CONCLUSIONS

- The H_2S adsorption capacity of AC Airpel Ultra DS is influenced by gas matrix composition and by the presence of oxygen in the gas mixture. In particular, CO_2 has a marked negative effect both in dry and in wet (R.H. 90%) conditions, leading to a relevant reduction of adsorption capacity. If 2% of O_2 is added to a gas mixture containing CO_2, the adsorption capacity enhances, reaching a value similar to that obtained in the same conditions but without CO_2. Therefore, the presence of small percentages of oxygen are able in part to neutralize the adverse effect of CO_2 in the case of H_2S adsorption. Moreover, the use of CH_4 as gas carrier instead of N_2 determines bigger adsorption capacity and this effect occurs both in dry an in wet conditions.
- N_2 adsorption-desorption measurements executed on the spent samples confirm the adsorption results. In particular, the samples that performed the runs with CO_2/N_2 or CO_2/CH_4 in the gas mixtures don't have residual micropore volume still available for further adsorption and also their B.E.T surface area is strongly reduced.
- The behavior of AC RGM1 changing gas matrix composition in dry conditions is partially different from AC Airpel Ultra DS: the presence of CO_2 in the inlet gas mixture reduces H_2S adsorption capacity, while the use of CH_4 as gas matrix doesn't determine an enhancement of performance.