Full Length Article

Comparison at laboratory scale of different types and configurations of commercial molecular sieves for one-step direct upgrading of biogas produced by anaerobic digestion

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ABSTRACT

In the present study we investigated, at laboratory scale, the possibility of upgrading biogas with a single step, without involving any pre- or post-treatment or multiple stage recirculation. This would allow small-scale AD plants to achieve convenient in-situ biomethane production entirely in accordance with REPowerEU objectives. In this respect, three commercial molecular sieves, i.Honeywell 13X, 4A, and 5A, were tested in two configurations in series (4A/13X and 4A/5A) in 25/75 v/v relative amounts. A control trap containing only the 4A molecular sieve using the same amount as the in series configuration was also used. Real biogas fed directly from the production reactors at atmospheric pressure was used in the experiments. The ability of the sieves to adsorb CO_2 in the proposed operational conditions was tested and proved. In particular, sample 4A was highly efficient in biogas upgrading (CO_2 retention rate of 42.4 g_{CO2}/kg, equivalent to 0.96 $mmol_{CO2}$/g) but its activity was limited to 18 days, while increasing the amount of material and combining different types of molecular sieves in series improved the performance. The possibility to regenerate and reuse the sieves was also proven.

1. Introduction

Biomethane is generally produced through biomass gasification or anaerobic digestion (AD) [1]. The latter is a biological process in which biodegradable matter is progressively degraded by distinct groups of microorganisms (bacteria and archaea), which function in a syntrophic relationship in an oxygen-free environment. As the last product of the process, microorganisms release so-called biogas, which is a mixture of CO_2 (30–50 % v/v), CH_4 (50–70 % v/v), and other trace gases (H_2S, NH_3, N_2, siloxanes, water vapor) depending on the nature of the input feedstock [2]. Afterwards, biogas can be upgraded to biomethane, which is discussed in the next paragraphs. As biomethane is the cheapest and most rapidly scalable renewable fuel currently available, an ambitious goal for annual European biomethane production has been set at 35 • 10^9 m^3 by 2030 (currently, 3 • 10^9 m^3 of biomethane is produced in the EU in one year [3]).

Residual liquid/semi-solid digestate, containing nutrient compounds and stabilized organic matter (e.g. humic and fulvic acids), is potentially suitable for agricultural uses [4], allowing the closure of the "circular" management of organic wastes, residues, and by-products [5]. Indeed, the EU Waste Framework Directive encourages AD as a recycling operation [6], and upgrading biogas to biomethane is financially incentivised by the REPowerEU Plan in order to reach the aforementioned annual production target.

CO_2 and trace gases are regarded as biogas impurities since their presence (i) reduces the overall LCV (especially CO_2) and (ii) makes biogas toxic and corrosive even in low concentrations (especially H_2S, NH_3, and siloxanes). For these reasons, cleaning and upgrading biogas are required prior to many uses (e.g., vehicle fuel or grid injection) [7].

Water scrubbing (WS), membrane separation (MS), pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA) and temperature swing adsorption (TSA) are the most commonly used upgrading technologies [8,9]. WS involves introducing biogas from the bottom of the scrubbing tower to contact the counter current flow of water. According to Henry's law, CO_2 is absorbed by water (efficiency higher than 98 %, favoured by low temperature and high pressure). Treated gas is then subjected to drying and refining stages for removal of water and volatile organic compounds (VOCs) in order to eventually obtain

biomethane. The preliminary steps of desulphurisation by treating with a solvent and removing of condensed moisture or particulates are also needed. In a variant of the WS technique, amine solvents can be used instead of water, as they are more selective in absorbing CO_2 at almost atmospheric pressure.

MS is based on the permeability of gas when it passes through a polymeric membrane due to the combination of thermodynamic (solubility) and kinetic (diffusivity) factors determined by the molecular structure of the gas and its interaction with the polymer matrix. In this case, first the water and H_2S which can worsen the membrane performance, have to be cleaned from the biogas. An activated carbon (AC) filter is generally used after this pre-treatment to retain the residual traces of H_2S and VOCs before upgrading the membrane. Besides the intense pre-treatment phase, multiple stages of gas recirculation are also carried out during MS process in order to achieve overall high CO_2 removal (about 98 %) and low CH_4 slips (<1%), and this increases the cost of the process [8].

PSA, VPSA, and TSA are all based on adsorption and have gained prominence in biogas upgrading [10]. The name of each process refers to the method applied for the regeneration of the absorbent: in PSA, pressure is lowered (e.g., from 6 to 1 bar) to release the compounds adsorbed in the pores of the material; in VSA, a vacuum is applied; and in TSA, the temperature is increased. They are all applicable for removal of CO_2 and other major impurities from biogas and are capable of handling wide ranges of operating conditions and scales [11]. The overall sustainability of these processes highly relies on the proper selection of adsorbent, which must be cost-effective, especially regarding to its regeneration, and must keep energy use to a minimum [12]. As H_2S (one of the most problematic biogas constituents) adsorption is generally irreversible, pre-treatment to remove it (as well as water) is required.

PSA units are compact, capable of achieving high purification levels, relatively cheap in terms of energy consumption, and safe and simple to operate. PSA is therefore very appealing but it has some issues in terms of CH_4 recovery efficiency (up to 4 % of "lost" CH_4) and the need to optimize the whole life cycle, as well as cost [8,13].

VPSA combines the advantages of PSA and vacuum swing adsorption (VSA, high adsorption pressure and vacuum–assisted regeneration). With respect to PSA, it usually leads to higher biomethane purity, yields, and regeneration efficiency, but at the cost of lower product recovery. TSA has the advantage of allowing operations [9–11].

Upgrading processes for biogas adsorption employ porous adsorbent media, specifically natural/synthetic zeolite and AC, and research is ongoing to find new or more advanced materials such as ultra-microporous (≤1.1 nm) ACs [10], carbon molecular sieves (CMSs) [14], and metal–organic frameworks (MOFs) [15]. For cost optimization, the use of low-cost natural materials such as clay, zeolite, fly ash, and wood ash is gaining interest [16].

The present study investigated the possibility at laboratory scale of upgrading biogas with a single step of treatment, without involving any pre- or post-treatment or multiple stage recirculation. This would allow small-scale AD plants to perform convenient in–situ biomethane production entirely in accordance with REPowerEU objectives. In this respect, three commercial molecular sieves, Honeywell 13X, 4A, and 5A, were tested in two configurations in series (4A/13X and 4A/5A) in 25/75 v/v relative amounts.

The selected adsorbents are among the most used commercial zeolites in industrial applications and are therefore easily available on the market at low prices. All selected zeolites are characterized by hydrophilic behaviour due to the negative charge of the 3D alumina–silica lattice which is balanced by the cations (sodium and/or calcium) hosted in the cavities of the zeolite structure. For this reason, gas molecules that exhibit polarity are preferentially adsorbed, and among them, water is the most strongly adsorbed molecule. From the most to the least polar, the order of gases covered in this study is: $H_2O > CO_2 \gg CH_4$. Zeolite 4A is the most hydrophilic compared to 5A and 13X so the first layers of molecular sieves in traps where the series configuration was used were

made of 4A to dehydrate the biogas. In this way, the adsorption capacity of the subsequent zeolite layers, 13X and 5A, was maximized for the adsorption of the remaining gases (mainly CO_2).

A control trap containing only the 4A molecular sieve using the same amount as the in series configuration was also used. Semi-continuous AD reactors fed with thickened sludge (TSL) and organic fraction of municipal solid waste (OFMSW) at laboratory scale have been directly connected to traps filled with molecular sieves. The main novelties of this paper are as follows: (i) real biogas feed directly from production reactors was used for the upgrading tests (instead of mixtures of pure gases, which are usually used according to most of the papers in the scientific literature), (ii) two different configurations of in series layers of zeolites were employed, and (iii) the upgrading was carried out without any pre-treatment step. As TSL and OFMSW are very common waste streams, recycling them into biomethane and digestate is essential in the context of sustainable waste management.

2. Materials and methods

2.1. Molecular sieves description

Adsorbing supports were supplied by UOP Honeywell plant located in Reggio Calabria (Italy). In particular, due to the ability to separate humidity and different gases from biogas, zeolites labelled 13X, 5A, and 4A were considered. These kinds of molecular sieves are inorganic aluminosilicate compounds generally used as solid adsorbents in industrial applications and are commercialized in different sizes in the form of beads (13X and 5A) and pellets (4A). Basically, the chemical formulas of these molecular sieves include Na, Al, and Si for 13X and 4A, which differ in their Si/Al molar ratio, and Ca, Na, Al, and Si for 5A. According to the pore size, nominally 1.0, 0.5, and 0.4 nm for 13X, 5A, and 4A, respectively, zeolite can adsorb different kind of molecules, such as water and CO_2, as in the present study. In addition, after drying, purification, separation and recovery of gases and liquids, the adsorbed substances can be desorbed and the molecular sieves regenerated.

2.2. Morphology and compositional analysis of molecular sieves

Complementary characterization techniques were used to characterize as-received (pure) and post-treatment (used) materials, to first confirm their structure type and then detect any modification after their use. The crystalline structure was investigated by powder X-ray diffraction (XRD) using a Bruker D2 Phaser with Cu Kα radiation at 30 kV and 20 mA. The attribution of peaks was made in accordance with the Joint Committee on Powder Diffraction Studies (JCPDS). The diffraction angle 2θ was varied between 5° and 80° in steps of 0.02° and a count time of 5 s per step. The morphology was evaluated by a Phenom Pro-X scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) spectrometer. EDX analysis was used to assess the element content, and at least 20 points of investigation were acquired under 3 magnifications for all samples. The thermal stability of the molecular sieves was investigated by using thermogravimetric analysis and differential thermogravimetric analysis (TGA-DTG). The measurements were carried out with 20 mg of sample under an air flow (30 mL/min) from room temperature to 1000 °C at a rate of 10 °C/min. All experiments were carried out twice.

2.3. Gas adsorption capacity of molecular sieves

The adsorption properties of molecular sieves were evaluated by measuring the adsorption of different gases (N_2, CH_4, and CO_2) using a purpose-made volumetric apparatus. The volumetric equipment consisted of 2 communicating sections separated by vacuum valves, the sample chamber, and a gas reservoir. The two sections were connected to a battery of flow controllers (Brooks Instruments). The vacuum in the volumetric equipment was obtained from a turbomolecular pumping

station (Edwards, T-Station). The vacuum in the two sections of the apparatus was measured by 2 capacitance gauges (Edwards Barocel 7025, pressure range = 1000–0.1 mbar, accuracy = 0.2 %). The sample temperature was measured by a thermocouple inserted directly into the sample holder (± 0.1 °C) and connected to a thermoregulator, which changed the sample temperature by a sock heater placed outside the sample chamber. Before each adsorption measurement, the sample was degassed at 150 °C in high vacuum (P = 10^{-4} mbar) for 12 h, then allowed to cool in high vacuum to 25 °C. When the sample temperature was stable, the gas in the reservoir (at pressure of 1 bar) was allowed to flow into the sample chamber and be adsorbed by the sample. As the volume, temperature, and pressure differences were known before and after connecting the valve to the sample chamber, the amount of adsorbed gas was calculated by Equation (1), where n_{in} and n_{fin} are respectively the initial and final (after adsorption) moles of gas, PM_{gas} is the molecular weight of the gas, and m_{sieves} is the mass of the molecular sieve.

$$\text{Gas adsorption} = \frac{(n_{in} - n_{fin}) \bullet PM_{gas}}{m_{sieves}} [\%] \qquad (1)$$

2.4. Semi-continuous AD test

A semi-continuous AD test was performed at laboratory scale by using the Bioprocess Control Bioreactor System (BPC Instruments). The system (Fig. 1) involved five 2 L glass reactors (designated as A, B, C, D, and E) internally equipped with a stirrer to ensure continuous mixing. The reactors were immersed in a thermostatic bath set at 35 °C (i.e., mesophilic conditions).

Each reactor was fed with the same mix of thickened sludge (TSL) and dried organic fraction of municipal solid waste (OFMSW), 50/50 based on volatile solids (VS). As operational parameters, organic loading rate (OLR) and hydraulic retention time (HRT) were set at 1 g_{VS}/L$\bullet$d and 21 days, respectively. TSL was periodically collected from the gravity thickener of a wastewater treatment plant (population equivalent to 30,000) located in Reggio Calabria (Italy). Samples were stored at 4 °C before use. OFMSW was prepared in the laboratory according to [17], then dried at 35 °C for 7 days and ground by a PULVERISETTE 15 cutting mill. Lastly, the inoculum used in the test came from previous AD experiments fed with similar substrates. The characterisation of the materials (pH, total solids, TS, VS, and volatile fatty acids (VFAs)) is reported in Table 1. Parameters were determined according to standard methods [18,19].

2.5. Direct upgrading system

Each semi-continuous AD reactor was connected by a Tygon® tube to

Table 1
Characterisation of materials.

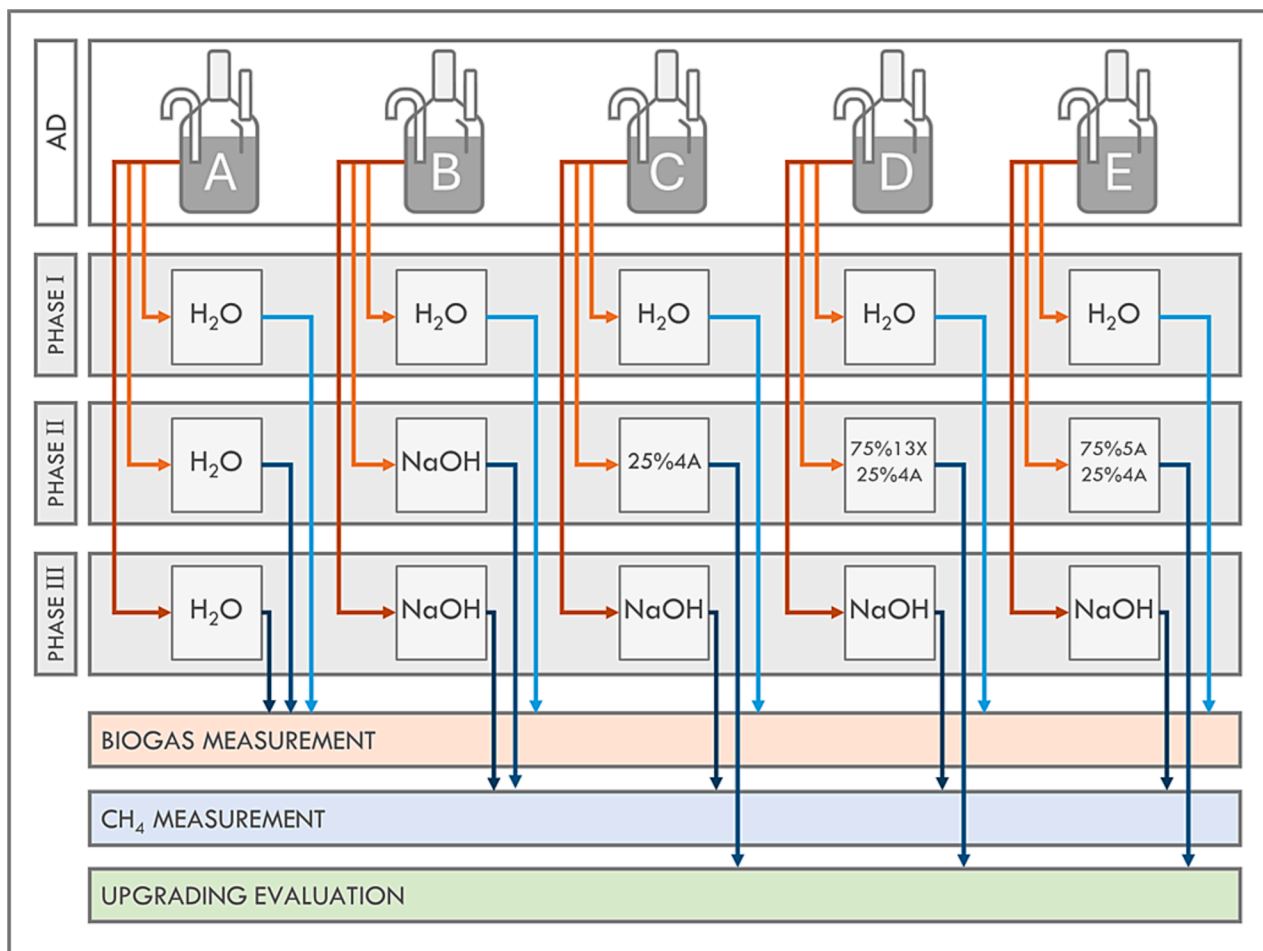| Material	TS [%]	VS [%TS]	pH	VFA [mg/L]
Inoculum	2.2 ± 0.23	68.2 ± 0.41	7.5	–
OFMSW*	21.7 ± 0.56	96.2 ± 0.13	6.1	–
TSL	1.7 ± 0.04	74.8 ± 0.28	6.5	226.4
	1.7 ± 0.22	76.7 ± 1.09	6.7	292.8
	2.4 ± 0.37	77.4 ± 0.10	6.7	218.7

* Referred to wet sample before drying.

Fig. 1. Schematic of experimental set-up.

a hermetically sealed glass beaker. Each beaker was labelled as the respective connected reactor (A, B, C, D, or E). Normally, beakers act as CO_2 traps. Here, they were filled with 400 mL of 3 M NaOH solution so that the CO_2 contained in the produced biogas would react with the NaOH while the remaining CH_4 volume was measured by an automatic measuring system. In this experiment, trap beakers were employed to simulate direct upgrading of biogas through commercial molecular sieves. Three distinct test phases were carried out:

(1) Traps were filled exclusively with distilled water for 11 days in order to verify regular and uniform biogas production in all reactors (start-up phase).
(2) Traps were filled with 400 mL of distilled water (trap A); 400 mL of 3 M NaOH solution (trap B); 115 g (25 % of total beaker volume) of 4A molecular sieve (trap C); 115 and 272 g (25/75 v/v) of 4A and 13X molecular sieves, respectively, placed in series (trap D); 115 and 310 g (25/75 v/v) of 4A and 5A molecular sieves placed in series (trap E) (Table 2). During this phase, gas exiting each trap was periodically captured with a 100 mL syringe in order to measure possible residual CO_2 content through a water displacement apparatus connected to an external 3 M NaOH trap. The second phase was interrupted when the CH_4 content in the gas leaving trap C (filled with 4A sieve) was lower than 90 %. This was observed after 43 days and was related to progressive exhaustion of adsorbent (see Table 3).
(3) Molecular sieves in traps C, D, and E were replaced with 400 mL of 3 M NaOH solution in order to verify that CH_4 production in all processes during the regime phase was still regular and uniform.

To determine the reliability of the results, the uncertainty of measured gas production in the case of a single semi-continuous AD test was considered on the order of 5–10 % according to an internal quality control test [20]. This seems an acceptable range when compared to the tolerance variability of ±25 % by the Italian standard (UNI/TS 11703:2018) for the experimental value of CH_4 potential for AD of microcrystalline cellulose with respect to the theoretical value. Finally, semi-continuous AD tests often imply a lack of replicates, as these experiments are labour-intensive, long, and quite expensive.

3. Results and discussion

3.1. Characterization of as-received molecular sieves

XRD analysis was used to assess the type of zeolite, and the recorded diffractograms are given in Fig. 2. For each sample, matching the observed peaks to patterns in the literature confirmed the featured crystalline structures. The main peaks of zeolite 13X were detected at 2θ = 6.1°, 10°, 15.5°, 20.1°, 23.3°, 26.7°, 30.5°, 31.0°, and 32.1°, the main peaks of zeolite 5A were observed at 2θ = 7.2°, 10.3°, 12.6°, 16.2°, 21.8°, 24°, 26.2°, 27.2°, 30°, 30.9°, 31.1°, 32.6°, 33.4°, and 34.3°. Finally, the characteristic peaks of zeolite 4A were observed at 2θ = 7.18°, 10.17°, 12.46°, 16.11°, 21.6°, 23.99°, 27.11°, and 29.94° [21,22].

SEM analysis of beads and pellets showed the composition of granules in the adsorbent phase, the zeolite crystals, and the binder, which was a clay. A homogeneous particle distribution was observed. In

Table 2
Volume and weight of molecular sieves used in traps.

Trap					
A	B	C	D		E
H_2O	NaOH 3 M	4A 25 % [*]	4A 25 % [*]	13X 75 % [*]	4A 25 % [*]	5A 75 % [*]
400 mL	400 mL	115 g	115 g	310 g	115 g	272 g

[*] Of beaker total volume.

Table 3
CH_4 content in gas exiting from molecular sieves traps.

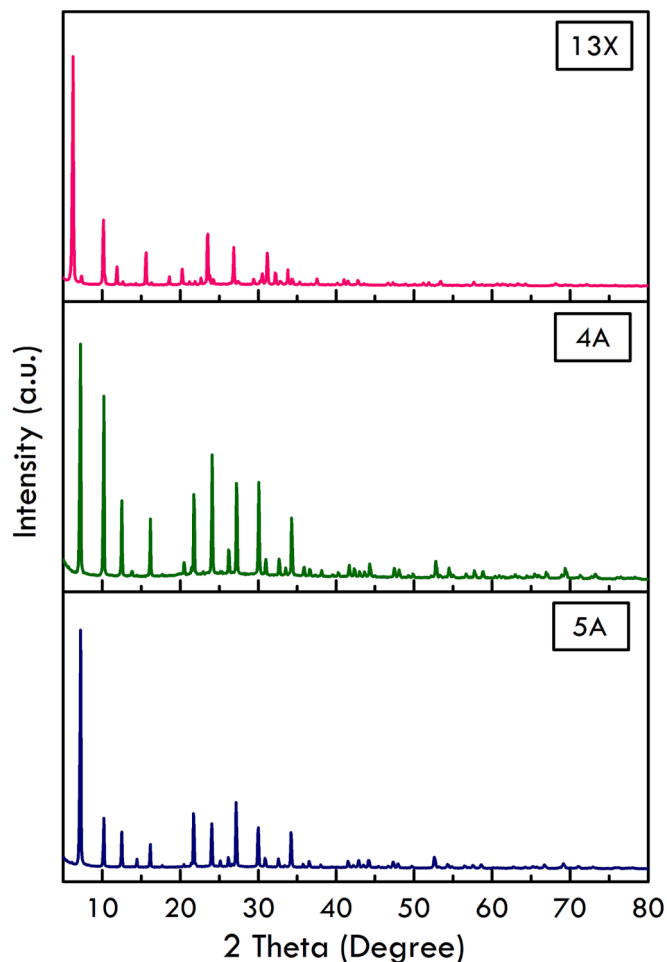| Trap	Time [d] [*]			
	8	18	28	30
C	100 %	98 %	91 %	87 %
D	98 %	99 %	95 %	95 %
E	98 %	98 %	100 %	97 %

[*] From the beginning of the second phase.

Fig. 2. XRD patterns of as- received molecular sieves: 13X, 4A and 5A.

particular, as shown in Fig. 3, an octahedral morphology was detected for zeolite 13X, whereas zeolites 4A and 5A were cubic crystals with rounded corners and edges [21]. As depicted in Fig. 3, EDX analysis of zeolite crystals allowed us to measure the elemental composition in terms of weight percentage, in accordance with their chemical formulas.

TGA-DSC analysis of all samples showed a stable structure with increasing temperature, with negligible weight loss (<2%) (not shown).

The adsorption of N_2, CH_4, and CO_2 by zeolites (Fig. 4) is given as the mean value of 10 measurements, and the values were as follows: 4A: 0.28 mmol/g for CH_4, 1.83 mmol/g for CO_2, and 0.16 mmol/g for N_2; 5A: 0.40 mmol/g for CH_4, 2.47 mmol/g for CO_2, and 0.28 mmol/g for N_2; and 13X: 0.33 mmol/g for CH_4, 2.53 mmol/g for CO_2, and 0.20 mmol/g for N_2. The adsorption properties of 13X, 5A and 4A samples confirmed the poor capacity for adsorption of N_2 and CH_4 gases (for both gases: 5A > 13X > 4A) and the good affinity for CO_2, proportional to the pore size and Si/Al ratio of the zeolite [23].

Reports in the literature [24–27] show CO_2 and CH_4 breakthrough adsorption capacity in the ranges of 3.0–6.0 and 0.5–1.0 mmol/g,
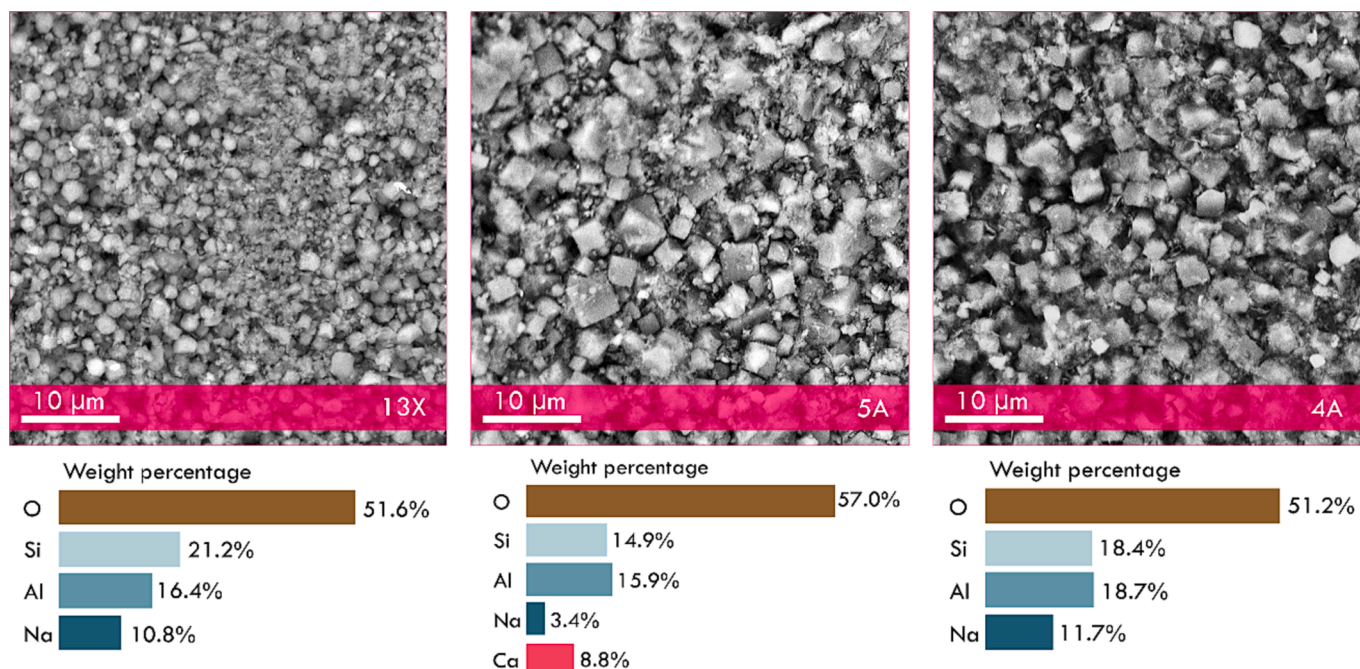
Fig. 3. SEM micrograph and EDX element weight percentage of as received molecular sieves: 13X, 5A and 4A.
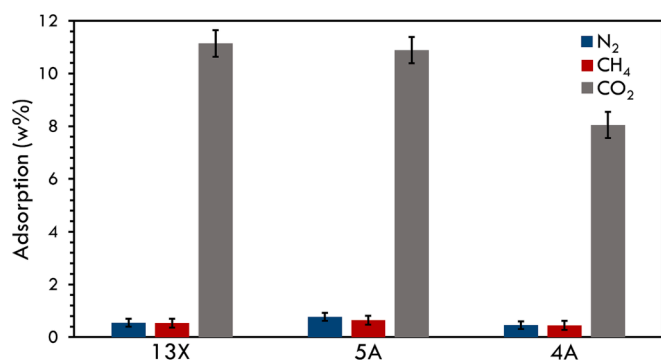

Fig. 4. Gas adsorption % of 13X, 5A and 4A samples.

respectively, for 4A, 13X, and 13XBF commercial molecular sieves at ambient temperature and atmospheric pressure. The lower values in these ranges refer to commercial, not binder-free, materials like those used in this work.

3.2. Semi-continuous AD test

The volume of gas exiting from traps throughout the three phases of the AD test divided by grams of VS loaded (gas yield) is depicted in Fig. 5a. The cumulative volume of gas produced during the entire experiment is shown in Fig. 5b. Vertical lines represent the end of each phase.

In the start-up phase, biogas production from all reactors was recorded as traps were filled with distilled water. As the experimental conditions were set equal for all reactors, as expected, all processes were run regularly and uniformly (Fig. 5a). Nevertheless, process B was the least biologically active (average daily biogas yield of 178.8, 178.1, 190.5, 194.6, and 199.7 NmL/g_{VS} for reactors A, B, C, D, and E, respectively). This was also observed during the third (and last) phase of the AD test, in which CH_4 production from reactors B, C, D, and E was compared (average daily CH_4 yield of 189.2, 207.3, 206.1, and 211.7 NmL/g_{VS} for reactors B, C, D, and E, respectively: Fig. 5a). The

implications of these results will be further discussed. Notably, the average daily CH_4 yields of the last phase of the test being larger than the biogas yields in the start-up phase is not contradictory, since AD performance is often better during the steady state due to the adaptation of the microbial consortium (see behaviour of process A in which only biogas production was monitored throughout the test).

From day 11 onwards (i.e., the beginning of the second phase), differences between processes were recorded. Reactor A obviously showed the highest daily gas yield, as the trap was still filled with distilled water, determining total biogas production (adsorption of CO_2 in water at room temperature is negligible). Conversely, daily gas yield of reactors B, C, D, and E was affected by CO_2 retained by the traps. Specifically, the gas exiting from trap B was basically the CH_4 produced by the reactor, as trap B contained the ordinary 3 M NaOH solution. On the other hand, gas leaving traps C, D, and E was the result of the traps in the tested biogas upgrading being those filled with molecular sieves (25 % 4A, 25/75 4A/13X, and 25/75 4A/5A); it has already been demonstrated that these reactors behaved very similarly in terms of CH_4/biogas production. What emerges from Fig. 5a, and more clearly from Fig. 5b, is that the volume of gas exiting from the traps was in the order C > B > D ≈ E. Regarding the process in reactor B as the control (thus the CH_4 production reference), based on that sequence it can be stated that traps D and E necessarily retained a higher quantity of CO_2 due to the further activity of the 5A and 13X molecular sieves in those traps, which were able to adsorb a larger quantity of CO_2 with respect to 4A, as demonstrated by the adsorption experiment reported above.

Gas exiting from the traps connected to reactors C, D and E was sampled four times during the second phase of the AD test in order to check the actual CH_4 content through an external 3 M NaOH trap. The results are reported in Table 2.

Interesting results were produced in the analysis of gas leaving trap C. From Table 2 it emerges that basically the entire volume of gas from trap C was CH_4 until day 18 of trap operation with the 4A sieve. Accordingly, it can be stated that the 4A sieve performed biogas upgrading quite well, and with values of CH_4 purity after PSA treatment consistent with those found in the literature (96–98 %) [28]. The 4A sieve was considered exhausted after about 30 days of usage, when the CH_4 content in the treated gas was lower than 90 %, a still satisfactory value. A CO_2 retention rate of 42.4 g_{CO2}/kg (equivalent to 0.96
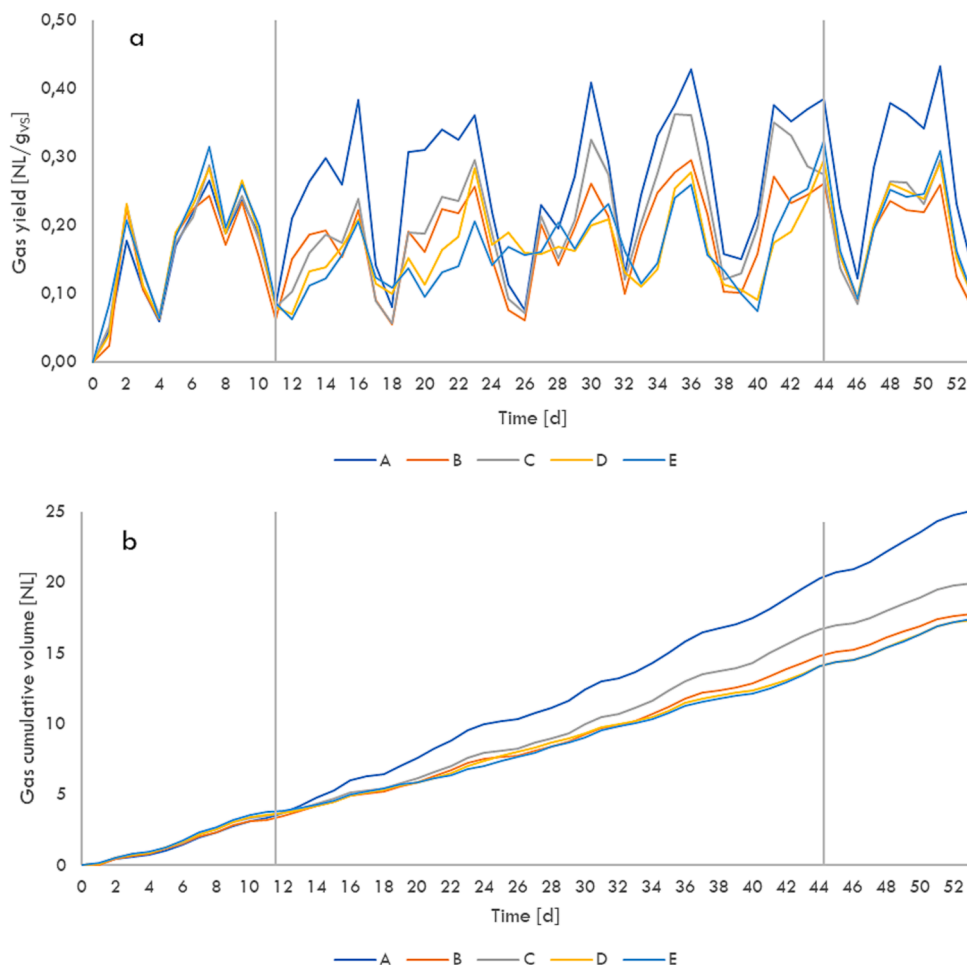
Fig. 5. (a) Gas yield and (b) cumulative volume of gas produced by each reactor-trap series.

$mmol_{CO2}/g$) for 4A was calculated by dividing the mass of retained CO_2 during the 18 days of trap C operations (6.6 g_{CO2}, or the difference between total cumulative volume of biogas in reactor A and reactor C; Fig. 5b) by the mass of the 4A sieve used to fill 25 % of the trap bottle (115 g). As already mentioned, the regularity of production in reactors A and C makes this calculation sufficiently reliable. Previously, the CO_2 retention capacity of the 4A sieve employed in the PSA process was estimated to be 0.81 $mmol_{CO2}/g$ in a pressure range of 1–5 bar [29]. The value of 1.16 $mmol_{CO2}/g$ was estimated considering the application of the 4A sieve under vacuum conditions (0.1–1 bar) [25].

In addition, the results for reactors D and E prove that the coupling of molecular sieves (4A/13X and 4A/5A) further increased the biogas upgrading with respect to reactor C. Indeed, in both cases, the lower cumulative gas volume shown in Fig. 5b was due to a higher quantity of retained CO_2 not only in the 25 % volume filled with 4A sieve but also adsorbed in the remaining volume (75 %) filled with 13X and 5A sieves. Accordingly, higher levels of CH_4, equal to 95 % and 97 % for reactors D and E were recorded (Table 2) even after 30 days of usage. The longer operation time proved the absence of saturation, as was recorded for reactor C. The higher quantity of molecular sieves (25/75 mixed type), as well as the type of sieve, 5A and 13X, which are characterized by higher CO_2 adsorption ability (Fig. 4), could explain these results, in terms of both higher CO_2 adsorption and CH_4 yield. These findings are further supported by the post-treatment characterization, discussed in the following.

It is noteworthy that a highly satisfactory level of biogas upgrading (~98 % of CH_4) was achieved in a single-step process, without any preliminary removal of moisture or H_2S [30,31]. Thus, it can be

reasonably supposed that the tested single-step biogas upgrading solution would be suitable for ordinary AD of a variety of substrates or co-substrates similar to those used in the tests (e.g. manures and lignocellulosic substrates). Furthermore, as traps for upgrading are directly connected to the respective reactors, high operating pressure is evidently not needed. This feature makes the tested upgrading solution particularly suitable for small-scale digesters.

The results are particularly promising since they were obtained by using real biogas but are similar to those obtained in the scientific literature with synthetic mixtures. Tabar et al. [32] operating a novel VPSA process comprising four columns, including two columns of CMS and two with zeolite Sr-ETS-4, with a simulated biogas (50 % CH_4, 40 % CO_2 and 10 % N_2), achieved CH_4 purity of 98 %. Another study [33] used zeolite 4A beads on a synthetic mixture of 60 % CH_4 and 40 % CO_2 to test a six-step PSA process (6 min of feed and 0.5 min of purge at 323 K); the obtained biomethane had a purity of 98.0 % with recovery of 89.2 %. Similar results were obtained when using materials different from zeolites. An experiment with zirconium MOF (UiO-66) for upgrading simulated biogas (30 % CO_2 and 70 % CH_4) [34] obtained purity of 98.2 % and recovery of 94.68 %. With the same gas mixture but using a ZIF-7 MOF as adsorbent, Abd et al. [35] obtained biomethane with purity of 97.1 % and recovery of 93.7 %. The following optimization analysis demonstrates that recovery could be increased to more than 95 % if the CH_4 content in the feed stream is higher than 60 %, the bed pressure is higher than 2 bar, and the outside wall temperature is less than or equal to ≤30 °C. Finally, upgrading a biogas mixture containing 32 % CO_2 and 68 % CH_4 using two beds, a four-step PSA, and spent coffee grounds (pre-treated by washing with distilled water and

drying overnight at 120 °C) as adsorbent, biomethane purity of 97.0 % and recovery of 95.4 % were recorded.

3.3. Characterisation of post-treatment molecular sieves

After the experiment, the post-treatment molecular sieves were further analysed, and the results were compared to those of the virgin (new) materials. XRD patterns remained unvaried, proving that, under the reported experimental conditions, no modifications occurred in the crystalline phase of samples. Similar results were found for the morphology, which was overall retained. On the contrary, EDX analysis showed the presence of carbon on the 13X sample, while s the elemental composition of 5A and 4A samples was unaltered. The presence of carbon was likely due to the CO_2 adsorption over the sieve. It has been discussed that CO_2 typically adsorbs by physisorption, with weak intermolecular interactions, but chemisorption of CO_2 also occurs on low Si/Al zeolites with monovalent cations, like A, X, and Y. This results in the formation of bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}) ion species, especially when catalytic amounts of water are present, as in this study [36]. Another important factor that determines CO_2 adsorption capacity is pore size. The adsorption of CO_2 on zeolites with high aluminium content (low Si/Al ratio), such as 4A and 5A, is mostly arranged over the superficial pores due to the small pore size (about 0.4 and 0.5 nm, respectively). This hinders diffusion along the internal cavities of the CO_2 and the eventually formed carbonate-like species that, being weakly bonded, are easily outgassed, as confirmed by the absence of carbon in the EDX analysis [23]. Moreover, the CO_2 capture may have been reduced over the 5A zeolite due to the partial poisoning of cations in the form of calcium hydroxyl and oxygen species, causing mass transfer resistance and diffusional limitations [37].

The water adsorbed in the analysed sieves was evaluated by TGA-DTG analysis, as shown in Fig. 6. The most significant weight loss could be attributed to the humidity on the surfaces and in the cavities of sieves, which began at approximately 50 °C and continued up to 350 °C. In this temperature range, the percentage of weight loss was 5.0 %, 4.6 %, and 7.1 % for 13X, 5A, and 4A zeolites, respectively. In particular, the weight loss of 4A was similar ($+/- 0.2$ %) for all the considered reactors (C, D, and E). For all samples, two water desorption peaks in the DTG curves were observed at low temperatures, below 100 °C, and 200–350 °C, indicating the existence of two types of water grafting in the structures [21]. Moreover, a comparison of the TGA curves of the 13X and 5A samples revealed no significant differences in total weight loss, whereas in the 4A sample the higher weight loss was mainly due to the higher contribution of humidity, in agreement with the stratification of molecular sieves in the experimental reactors. Finally, after the early weight loss, samples were stable up to 1000 °C.

Adsorption tests were carried out on the post-treated samples to investigate their regeneration potential. The tests confirmed the possibility to restore and reuse all of the analysed molecular sieves. Indeed, it was proved that, under desorption conditions in low-temperature regeneration, as shown by TGA-DSC analysis, or the mild vacuum conditions used in adsorption measurements, adsorbed gas can easily be desorbed, thanks to the low physical/chemical interactions with the zeolitic structures. In addition, even adsorbed carbon-like species can be removed concurrently with water/humidity desorption, as they are strictly correlated with one another. As demonstrated by SEM-EDX analysis of regenerated 13X sieve (results not shown), there was no evident carbon content on its surface, suggesting that desorption of carbon-like species and humidity was overall achieved. Moreover, in the subsequent cycle of adsorption measurements, regenerated molecular sieves had the same gas adsorption ability of virgin ones. Thus, it would be advantageous to implement a self-regeneration system that can recover sieve efficiency using the low thermal heat generated by the biogas itself or, at the most, exploiting renewable energy sources (e.g., hot air generated by a solar turbine), finally ensuring a fully sustainable process.

4. Conclusions and future prospects

The potentiality for using different kinds of molecular sieves for the upgrading of biogas was clearly evidenced. The ability of these sieves to adsorb CO_2 in the proposed operational conditions was tested and proved. In particular, the 4A sample was highly efficient in biogas upgrading (CO_2 retention rate of 42.4 g_{CO2}/kg, equivalent to 0.96 $mmol_{CO2}$/g), but its activity was limited over the time of the experiment (18 days). Further improvement was achieved by increasing the amount of material in the traps (from 25 % to 100 % of total trap volume) and combining different types of molecular sieves, namely 4A/13X and 4A/5A (both 25/75 v/v), in order to obtain higher and constant biogas upgrading for the whole testing time (30 days) without causing significant changes in the zeolite structure. The possibility to regenerate and reuse this kind of materials was also proven.

The features of the proposed upgrading solution (use of common commercial materials, application of low pressure, and absence of preliminary treatments) coupled with satisfactory process performance, make biogas upgrading potentially economically viable, particularly for small-scale digesters.

Nevertheless, future research is needed to investigate the most appropriate modality for the regeneration of exhausted sieves and evaluate the effects on the sieves (in terms of adsorption efficiency) during multiple regeneration cycles in the long term.

CRediT authorship contribution statement

Lucio Bonaccorsi: Writing – review & editing, Supervision, Methodology. **Filippo Fazzino:** Writing – original draft, Methodology, Investigation, Data curation. **Antonio Fotia:** Writing – original draft, Methodology, Investigation, Data curation. **Angela Malara:** Writing – original draft, Methodology, Investigation, Data curation. **Altea**
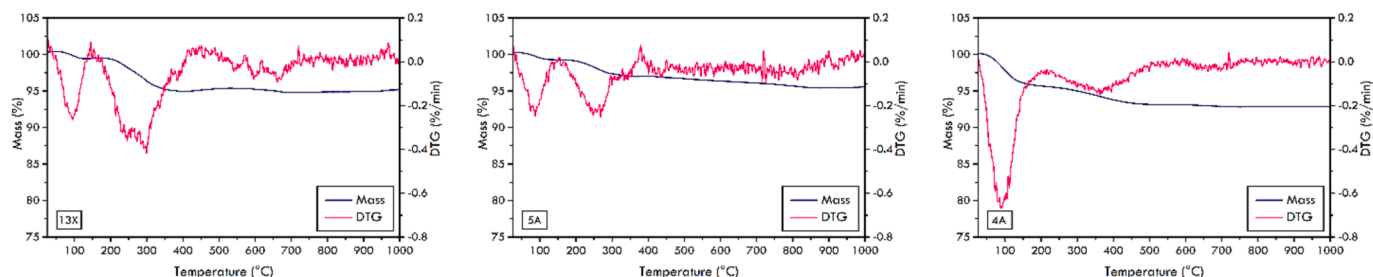
Fig. 6. TGA-DTG graphs of post-treated 13X, 5A and 4A samples.

Pedullà: Writing – original draft, Methodology, Investigation, Data curation. **Paolo S. Calabrò:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Paolo S. Calabro reports financial support was provided by Government of Italy Ministry of Education University and Research.

Data availability

Data will be made available on request.

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